Two-stage drawing of high-molecular-weight polyethylene reactor powder

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Polyethylene reactor powders with molecular weight ranging from 0.16×10^6 to 14.9×10^6 synthesized under various conditions have been subjected to drawing. The powders were compacted at controlled pressures and temperatures below their melting points. Compaction into plates was followed by two-stage solid-state drawing. The first stage was solid-state extrusion, the second was tensile drawing, both at controlled rates and temperatures below the melting point. It is found that the drawability of reactor powders depends sensitively on the polymerization temperature and conditions. Samples synthesized at 85°C in a slurry are highly drawable. In contrast, powders obtained at 30°C in the gas phase are not readily drawn. Molecular weight is found not to be the dominant factor in determining the drawing of reactor powder. Rather, it is the synthesis conditions, as they influence the interphase regions between crystals, that appear to control the limits of drawing. For the most favourable case among these samples, namely higher molecular weights and higher polymerization temperature, total draw ratios of nearly 100 and tensile moduli of 75 GPa were attained.

(Keywords: polyethylene; drawing; molecular weight)

INTRODUCTION

Drawn polymers of ultrahigh molecular weight can have unusual properties. Examples are improved mechanical properties, better impact strength and tensile strength and high modulus. The melt index of ultrahigh-molecular-weight polymers approaches zero, limiting their processing by the usual methods. Attempts have been made to overcome this difficulty. One route is to use powder processing. The well known example is the processing of polytetrafluoroethylene (Teflon). This polymer is treated as follows: first it is compacted in powder form, then heated to the gel state, shaped and subsequently solidified[1]. Porter *et al.* have demonstrated that a commercial ultrahigh-molecular-weight polyethylene (UHMWPE) reactor powder can be drawn up to a draw ratio (*DR*) of 60 at 128°C by solid-state coextrusion[2,3]. In contrast, conventional extrusion of UHMWPE of melt-crystallized morphology proceeds only to an extrusion draw ratio of 5, even as high as 136°C. Kanamoto *et al.* have reported that by two-stage drawing UHMWPE reactor powder can be drawn up to 77 times at 120–135°C. Such highly drawn films exhibited tensile moduli up to 107 GPa[4]. This high drawability at below the melting point of PE is due to reduced molecular entanglement.

In this study, a two-stage drawing technique is used to evaluate the ductility of PE reactor powders. The samples are those from Union Carbide. They cover nearly a 100-fold range of molecular weights, with a molecular-weight series available for most of the specific polymerization conditions. The samples and their molecular weights are shown in *Table 1*. It is found that certain classes of these PE reactor powders are highly ductile and that high tensile moduli are achieved for the highly drawn films of intermediate molecular weights.

EXPERIMENTAL

The as-received UHMWPE reactor powders were compression-moulded into a plate 1 mm thick at 150 kg cm^{-2} and 120°C. This is 20°C below the d.s.c. melting peak temperature. The goal of compression is to maximize short-range interactions for consolidation of lamellar crystals and short-segment interactions and to elimin-

Table 1 Molecular weight, ductility and tensile modulus obtained for two-stage drawing of PE reactor powder

Sample identification code	M_v ($\times 10^{-6}$)	$TDR_{\max}$[a] (135°C)	Modulus, max. (GPa)
HE 1900	3.96	104	123
S30–5.9	5.95	9	–
S30–12.4	12.42	6	–
S30–14.9	14.92	24	–
S30–2.9	2.86	15	–
S60–1.6	1.57	8	–
S85–4.8	4.80	98	75
S85–2.0	2.00	85	57
S85–1.0	0.96	90	62
S85–0.3	0.30	50	49
S85–0.9	0.93	–	–
GP30–1.9	1.93	7	–
GP85–0.9	0.96	22	–
GP85–0.2	0.16	19	–
GP85–1.2	1.16	9	–

[a] *TDR*, the total draw ratio, is *EDR*, the extrusion draw ratio, multiplied by the final tensile draw ratio

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ate voids, without activating longer-range and higher-temperature interactions such as the generation of entanglements.

A 4 mm wide strip of the compacted UHMWPE powder plate was drawn by our two-stage drawing method[4]. For the first-stage drawing, a compacted PE strip was sandwiched between split billet halves of high-density polyethylene and the assembly coextruded at 120°C through a conical bronze die having an entrance angle of 20°. The extrusion draw ratio (*EDR*) of the coextrudate was determined from the displacement of an ink mark preimprinted on the strip surface. For the second-stage drawing, extruded films of 2–4 cm length were drawn by a tensile force in an Instron tensile tester model 1321, equipped with a temperature chamber. This second-stage drawing was done at a constant temperature of 135°C and strain rate of 200% $\min^{-1}$. The total draw ratio (*TDR*) of the drawn samples was calculated by multiplying *EDR* and *DR* achieved in the second stage. The tensile moduli of drawn films were measured at room temperature at a strain rate of $1 \times 10^{-3}\ \mathrm{s}^{-1}$. The modulus was determined from the slope of the stress–strain curve at a low (<0.1%) strain.

The melting point and heat of fusion of the drawn films were measured on a Perkin–Elmer DSC-4 differential scanning calorimeter at a heating rate of 2°C $\min^{-1}$ to avoid the superheating problem.

RESULTS AND DISCUSSION

Solid-state coextrusion

The UHMWPE powder compacted at lower temperatures is white, opaque and brittle. D.s.c. measurement shows that the thermal behaviour does not change up to the chosen preform compression temperature of 125°C. After coextrusion it becomes more flexible and more transparent with increasing *EDR*. As found before, solid-state coextrusion can even impart flexibility to brittle polystyrene[5]. This change is due to formation of a fibre morphology from the aggregates of reactor powder. To achieve a high draw, a two-stage drawing technique had been employed, i.e. using the extrudate for a second-stage drawing. The morphology of the first-stage extrudate is generally found to be deformable by the second-stage tensile drawing.

The influence of EDR on TDR

For maximum two-stage drawing, the preferred first step is coextrusion to a low *EDR* of about 6. This step markedly improves the drawability and the efficiency of drawing for the second-stage tensile drawing. This conclusion is also consistent with the study of drawing of PE single-crystal mats[4]. In the present work, coextrudates with an *EDR* of 4, 6 and 8 were restudied. It was found that a higher final tensile draw ratio was obtained using an extrudate of *EDR* = 8 in the first stage. Note that for sample PE S85–4.8 a *TDR* of 64 was obtained at 130°C from the coextrudate with *EDR* = 6. For the coextrudate of *DR* = 4, the highest *TDR* was less; 54 for the same conditions. The drawability of reactor powder is also increased at higher drawing temperature, yet still below the melting point. The highest *TDR* obtained for any reactor powder (*TDR* = 98) was obtained by drawing at 135°C from coextrudates of *DR* = 8. For direct comparison with our previous data on Hercules Hifax 1900 (HE 1900), coextrudates with *EDR* = 6 at 135°C were used for all other reactor powder samples; see *Table 1*.

Tensile moduli

Tensile moduli as a function of total *DR* for compacted PE S85–4.8 reactor powder are shown in *Figure 1*. It can be seen that modulus increases rapidly with *DR* up to 60 GPa at *DR* = 80. It is interesting to find that one curve fits all modulus–*TDR* data obtained from extrudates with different initial *EDR* and at temperatures of 130 and 135°C, respectively. This means that, under these circumstances, the molecules have an equal efficiency of chain extension and orientation. At the highest *TDR*, the modulus drops, probably indicating the onset of microvoid formation. *Figure 1* shows apparently void-free draw to over 70 GPa.

Thermal behaviour

The melting peak temperature and heat of fusion as a function of *TDR* for drawn S85–4.8 at 135°C are shown in *Figures 2* and *3*, respectively. The same trend is seen as noted by Kanamoto *et al.* in their study of the HE 1900 reactor powder[4]. The highest heat of fusion and peak melting point achieved for the PE S85–4.8 are the same as they obtained. From the melting behaviour and heat of fusion of HE 1900 after compression moulding, Kanamoto concluded that a significant amount of less stable structure present in the reactor powder reorganized during compression. In our study, no significant change of thermal behaviour has been found on moulding at 125°C. This may be due to the fact that compression moulding was done at 10°C lower than in the previous

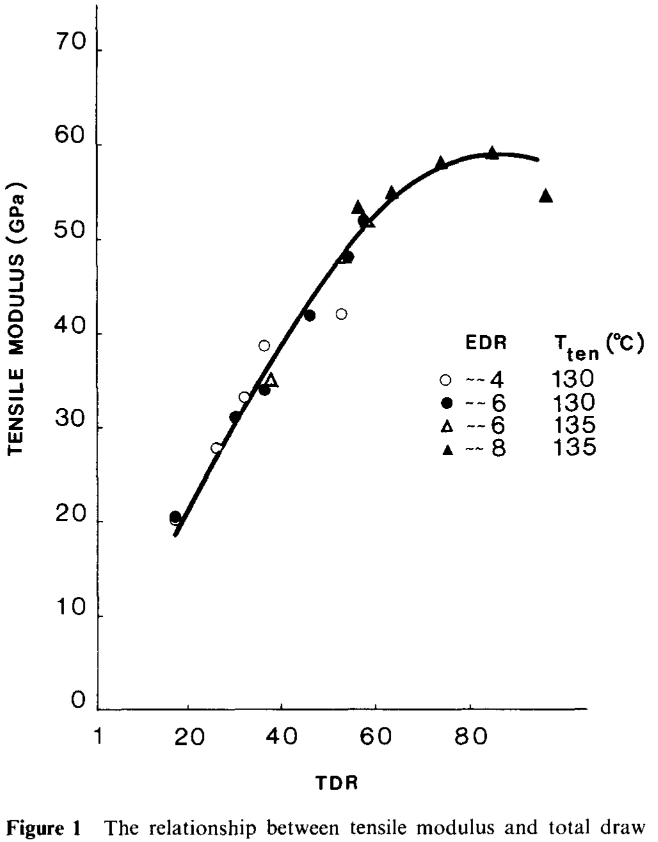

Figure 1 The relationship between tensile modulus and total draw ratio for S85–4.8. *EDR* is the draw ratio of coextrudate; T_{ten} is the temperature for tensile drawing

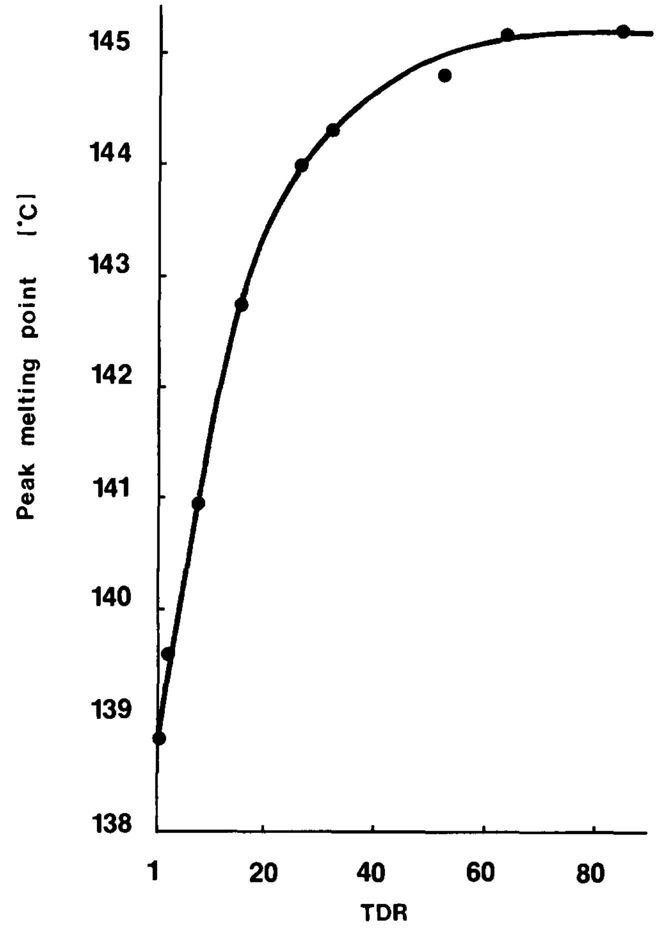

Figure 2 The relationship between the peak melting point and total draw ratio for sample S85–4.8

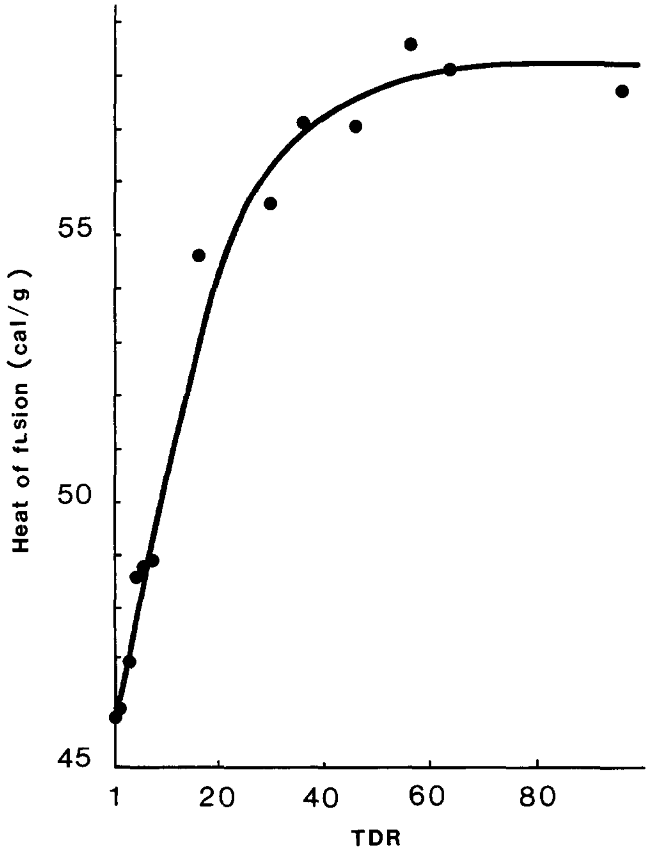

Figure 3 The relationship between the heat of fusion and total draw ratio for sample S85–4.8

study. On drawing the compacted powder, both melting temperature and heat of fusion increase with *TDR*, and the melting peak also becomes sharper (see *Figure 4*), each reaching a limit at a *TDR* of about 50.

As desired and anticipated, the two-stage drawing technique was efficient for achieving chain orientation and extension of PE[4]. These highly drawn polyethylenes contain a variable percentage of fully extended-chain crystals formed as a result of the mechanical action applied to the polymer films. The drawn morphology may be considered to be composed of a percentage of extended-chain crystals that increases with drawing, coexisting with conventional chain-folded crystals.

The peak of the d.s.c. melting curve is where the majority of the crystallites melt rather than the higher temperature at which the final crystallites melt[6]. If annealing is performed at the melting peak temperature, the less perfect crystals melt first, leaving the most perfect intact. In a test for the presence of extended-chain crystals, annealing experiments were carried out at the melting peak of PE S85–4.8 drawn to a *TDR* of 36. Annealing was conducted from 1 to 10 min; after cooling and subsequent reheating, two peaks were obtained. One is as usual at 133°C; the other, depending on the annealing condition, is at about 146 ± 0.5°C, equal to the equilibrium melting temperature of polyethylene[7–9] (see *Figure 4*). Other experiments have been done on films with a *TDR* of 52 and for PE S85–2.0 of *TDR* = 85. Two peaks for all samples were obtained and at the same temperature. For the starting nascent UHMWPE powder after annealing, two melting peaks can also be obtained, but the higher-temperature peak appears only at 141°C (*Figure 5*). This shows that, during annealing, only partial melting occurs, and that crystals that did not melt during the annealing experiment did not do so due to their extended chains. The area under the second peak slowly decreases with time, together with a gradual shift in the position of the maximum towards higher temperature. However, a high melting temperature, 146°C, is never seen after the first melting. One conclusion that could be drawn is that two-stage drawing produces a fraction of crystals with fully extended chains. This has not been seen in our previous studies[10]. Yet a similar

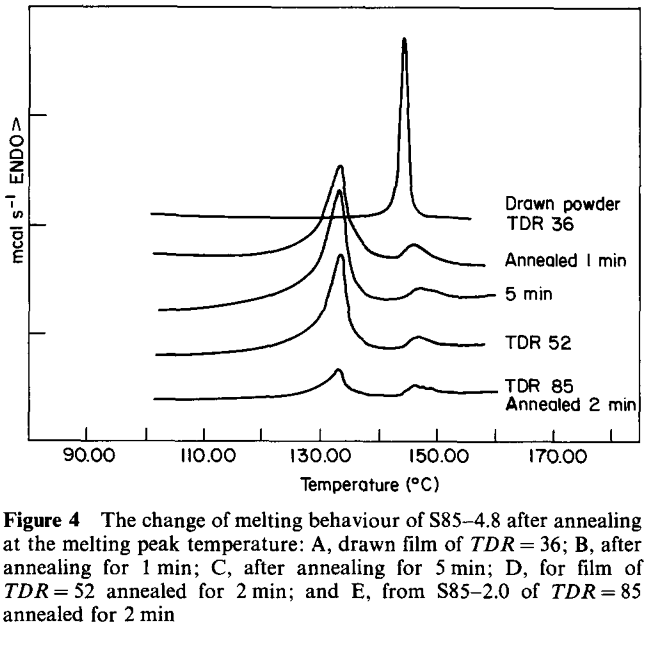

Figure 4 The change of melting behaviour of S85–4.8 after annealing at the melting peak temperature: A, drawn film of *TDR* = 36; B, after annealing for 1 min; C, after annealing for 5 min; D, for film of *TDR* = 52 annealed for 2 min; and E, from S85-2.0 of *TDR* = 85 annealed for 2 min

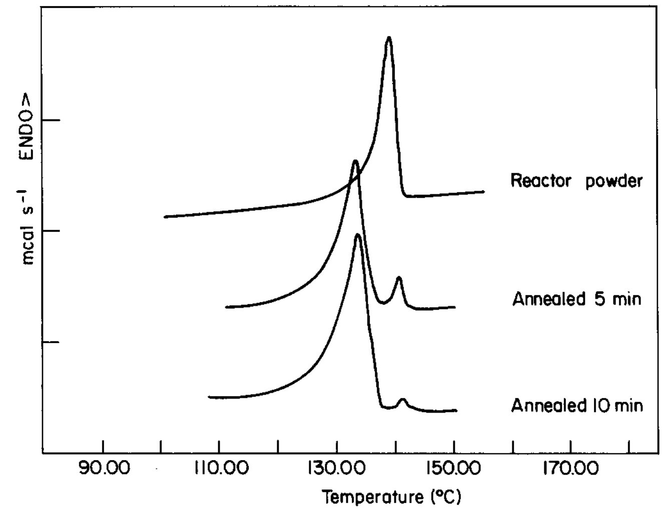

Figure 5 Thermogram of S85–4.8 nascent powder: A, original reactor powder; B, annealed for 5 min; and C, annealed for 10 min

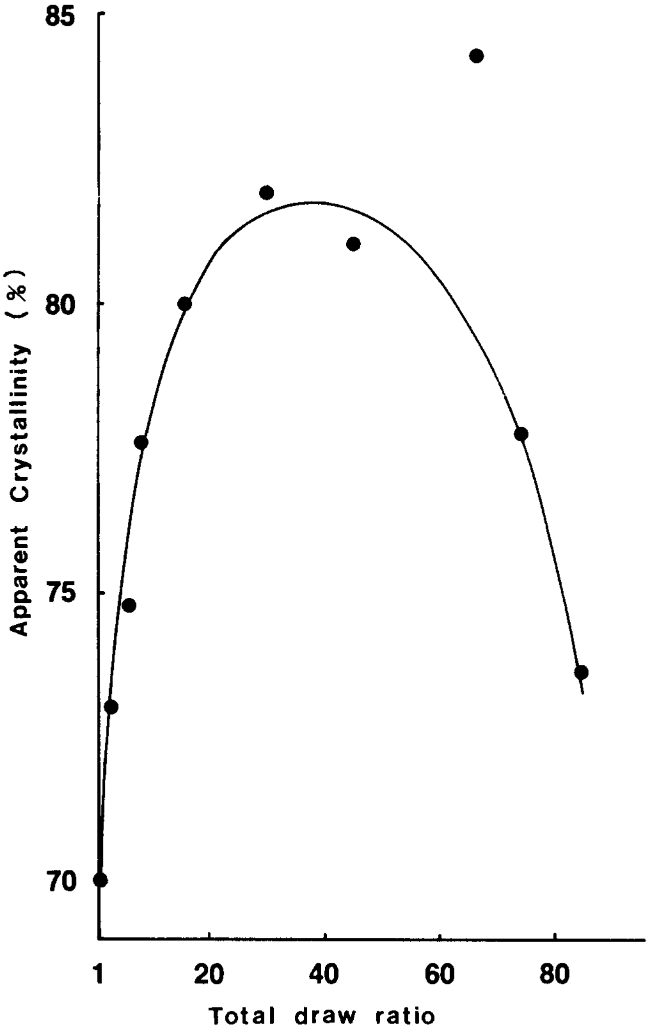

Figure 6 The change of crystallinity with *TDR* measured by density at 23°C

result has been reported by Chanzy *et al.* for the UHMWPE nascent powder. In their case, the high-temperature peak was at ~145°C[11].

Change of crystallinity of UHMWPE with TDR

The change of crystallinity of UHMWPE reactor powder with *TDR* was followed by changes on drawing in heat of fusion and densities. The heat of fusion increased sensitively with *TDR* (*Figure 3*). A heat of fusion of 58 cal g^{-1}, i.e. 84%, was obtained at *TDR* ≃ 60. There is a limiting high crystallinity at high *TDR* (see *Figure 3*), but, in density measurements, when the *TDR* was higher than 60, the density dropped markedly (see *Figure 7*). The density decrease at high draw thus shows that force causes the fibrous structure to slip and split into fibrils. In consequence, microporosity occurs and the apparent density decreases at the same time. From *Figure 7* it can be seen that the higher the *TDR*, the lower the apparent density. The filled circle is for HE 1900.

X-ray measurement

Wide-angle X-ray diffraction patterns of the (1 1 0) and (2 0 0) reflections of an original compacted powder and its drawn counterparts are shown in *Figure 8*. The highly drawn films, of *TDR* = 36 to 98, show a similar and high crystal orientation. The crystal structure for this sample is found to be exclusively orthorhombic. Crystal orientation increases rapidly to saturation with *TDR*. This is consistent with results on drawing of HE 1900 reactor powder[4].

Ductility of UHMWPE

All UHMWPE reactor powders were drawn as-received and under the same conditions. The highest *DR* attained for individual reactor powders is listed in *Table 1*. This table perhaps shows for the first time that the polymerization temperature and conditions have a major influence on subsequent ductility. The samples polymerized in slurry at 85°C have the greatest drawability.

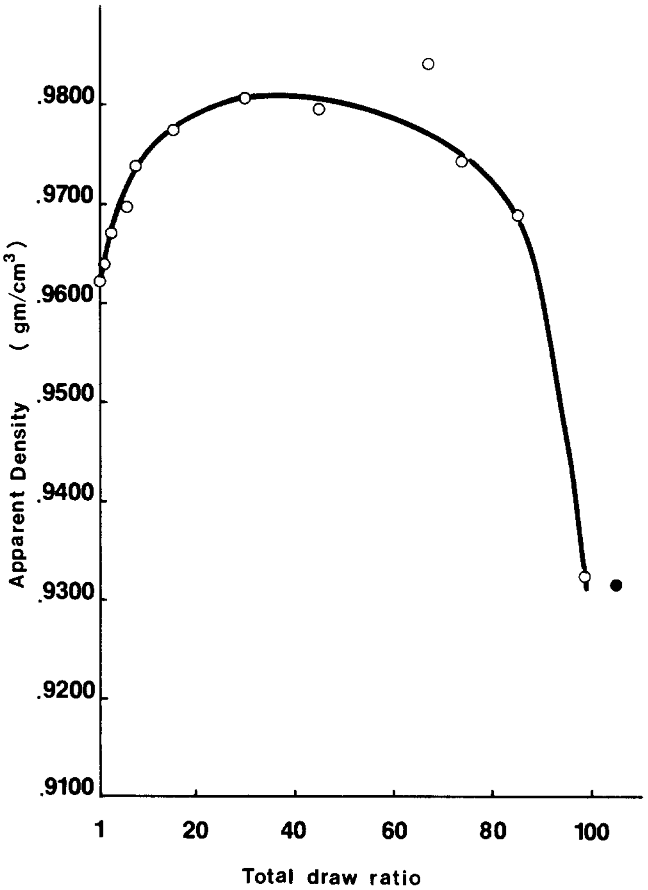

Figure 7 The change of sample density with *TDR*

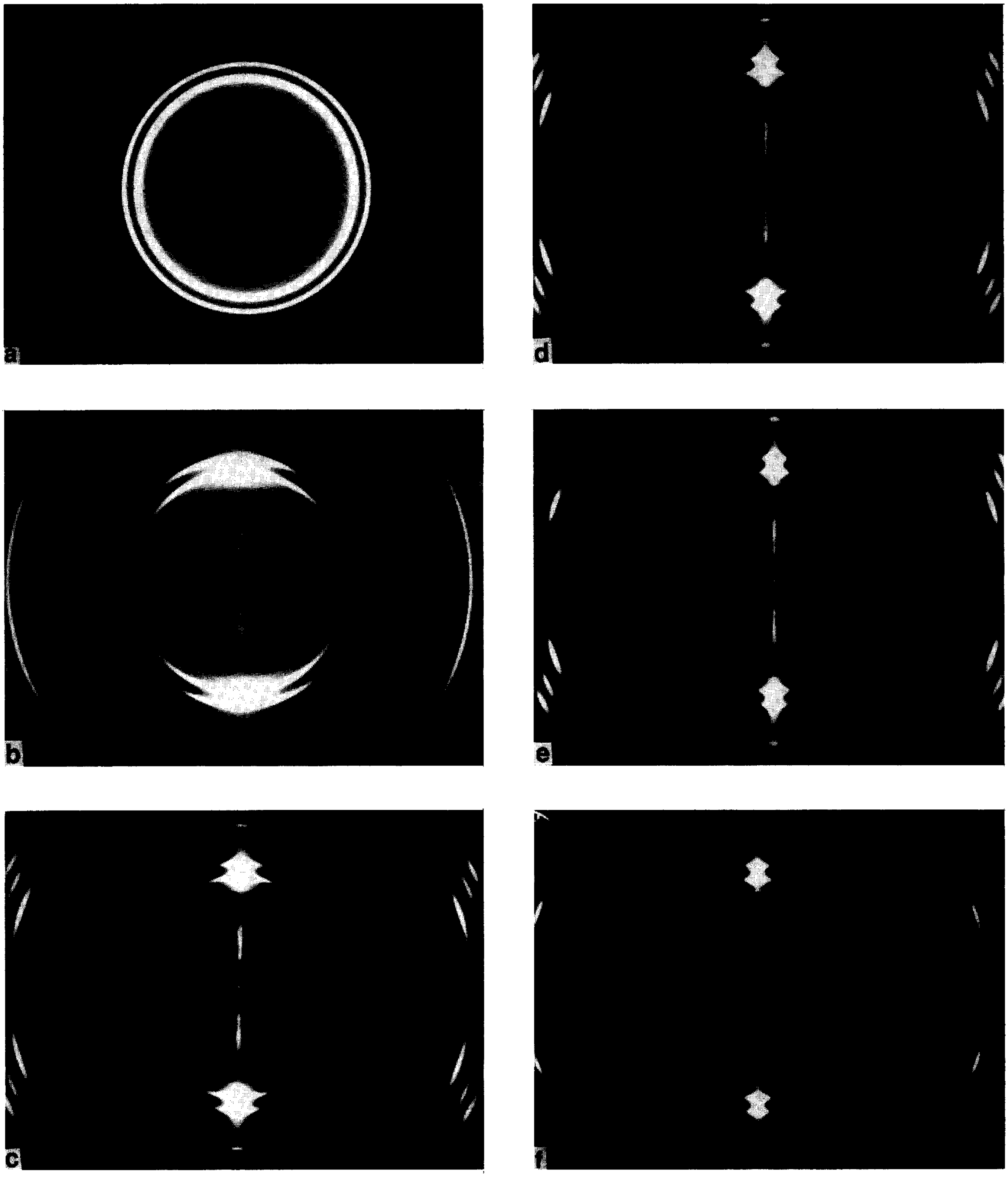

Figure 8 The X-ray reflection patterns for sample S85–4.8: (a) initial powder; (b) sample with $TDR = 8$; (c) $TDR = 16$; (d) $TDR = 36$; (e) $TDR = 64$; (f) $TDR = 98$

Samples synthesized at lower temperature and in the gas phase do not draw well under these conditions. PE GP30–1.9, synthesized at 30°C in the gas phase, cannot even be obtained through a second-stage draw. Smith also studied virgin powder processing. He found that the maximum draw ratio drastically increases from 19 to more than 40 upon decreasing the polymerization temperature from 25 to −40°C[12]. The trend differs from ours! The likely reason is that the polymerization catalysts are different, as are the temperature ranges.

From limited past experience, it has been deduced that PE molecular weight has a major influence on ductility. The maximum draw ratio for solution-grown UHMWPE crystals with molecular weight of 2×10^6 is about 350[13]. Under similar processing conditions, the molecular weight has been found here to have less influence on the drawability of nascent reactor powder. Samples of PE S30–2.9, S85–2.0 and GP30–1.9 have almost the same molecular weight, but their maximum DR ($DR_{\max}$) differ markedly (see *Table 1*). On the other hand, the maximum draw ratios for samples synthesized at 85°C in a slurry, with different molecular weights, differ little: PE S85–4.8 has molecular weight of 4.8×10^6 and its $DR_{\max}$ is 98; and PE S85–1.0 with MW of 0.96×10^6 has $DR_{\max}$ of 90 (see *Table 1*). The major differences are probably due to the different initial morphologies in the reactor powders.

CONCLUSIONS

The drawability of as-received UHMWPE nascent reactor powder is found to depend sensitively on the polymerization temperature and conditions. Samples synthesized at 85°C in slurry are found to be highly ductile. In contrast, reactor powders obtained at 30°C in the gas phase are not readily drawn. The distinctions of synthesis are retained on conducting all three processing steps below the melting point of the reactor powders. The steps are powder consolidation under pressure, solid-state extrusion followed by tensile drawing.

The observed presence of monoclinic crystals in some reactor powders infers crowding, leading to deformation during chain growth on the catalyst surface. This crowding is probably associated with some overlap and/or entwining of chains, which may restrict subsequent drawing.

REFERENCES

1 Rudner, M. A. 'Fluorocarbons', Reinholt, New York, 1958

2 Zachariades, A. E., Watts, M. P. C., Kanamoto, T. and Porter, R. S. *J. Polym. Sci., Polym. Lett. Edn* 1979, **17**, 485

3 Pawlikowski, G. T., Porter, R. S. and Mitchell, D. J. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1865

4 Kanamoto, T., Ohama, T., Tanaka, K. and Porter, R. S. *Polymer* 1987, **28**, 1517

5 Zachariades, A. E., Sherman, E. S. and Porter, R. S. *J. Polym. Sci., Polym. Lett. Edn* 1979, **17**, 255

6 Southern, J. H., Porter, R. S. and Bair, H. E. *J. Polym. Sci. (A-2)* 1972, **10**, 1135

7 Glenz, W. and Peterlin, A. *J. Polym. Sci. (A-2)* 1971, **9**, 1243

8 Ergoz, E., Fatou, J. G. and Mandelkern, L. *Macromolecules* 1972, **5**, 147

9 Lauritzen, J. I. Jr and Hoffman, J. D. *J. Appl. Phys.* 1973, **44**, 4340

10 Mead, W. T. and Porter, R. S. *J. Appl. Phys.* 1976, **47**, 4278

11 Chanzy, H. D., Bonjour, E. and Marchessault, R. H. *Colloid Polym. Sci.* 1974, **252**, 8

12 Rotziner, B. P., Chanzy, H. D. and Smith, P. to be published

13 Zachariades, A. E. and Kanamoto, T. 'High Modulus Polymers' (Eds A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, 1988, p. 307