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

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A two-stage drawing technique has been successfully applied for drawing of ultra-high molecular weight polyethylene reactor powder. Compacted powder films prepared below the ambient melting point of the initial powder was solid-state coextruded to a low extrusion draw ratio of 6 followed by tensile drawing at elevated temperatures of 120–135°C. The drawability for the second-stage tensile drawing and the uniformity of the resultant ultradrawn films were significantly affected by the drawing temperature and rate. The initial powder and drawn films were characterized by the tensile measurements, differential scanning calorimetry (d.s.c.) and X-ray diffraction. The results show the characteristic morphology of the reactor powder. Thus, the compacted powder films were effectively drawn up to a draw ratio of 77. Such highly drawn films exhibited tensile moduli up to 107 GPa. As the samples fractured by a repetitive partial rupture at the edge of cramp, the observed tensile strength at break were fairly low and in the range 1.0–1.4 GPa at a draw ratio range of 35 to 77.

(**Keywords:** reactor powder; polyethylene; solid state extrusion; modulus; strength)

INTRODUCTION

Ultra-high modulus and strength fibres and films of polyolefins have been prepared by uniaxial drawing of ultra-high molecular weight polyethylene (UHMW-PE)[1–4] and polypropylene (UHMW-PP)[5,6] from gel and single crystal aggregates. Among these techniques, solid-state coextrusion[7], developed by Griswald, Zachariades and Porter, followed by tensile drawing of single crystal mats of UHMW-PE[3] and UHMW-PP[5] has been shown to produce superdrawn films with tensile moduli and strength approaching the theoretical maximum values reported for the crystal for each of the two polymers. These processes involve the dissolution of polymers in some solvents followed by gelation or crystallization to improve the drawability of the high molecular weight polymers.

Recently, Smith *et al.*[8] have proposed a new route to high modulus and strength films by ultradrawing of virgin UHMW-PE films prepared under controlled reaction conditions. Porter, with Pawlikowski and Mitchell[9], have demonstrated that a commercial product of UHMW-PE reactor powder could be drawn up to a draw ratio (*DR*) of 60 by solid-state coextrusion alone, as a proposed modification of our superdrawing of single crystal mats[3,5]. Such highly drawn films showed tensile moduli up to ~60 GPa. These new processes markedly simplify the previous ultradrawing processes of UHMW-PE as these do not involve the solvent treatments before drawing which have been the key process for the latter to improve the deformability of high molecular weight polymers. In our previous studies[3,5,10], it has been found that a two-stage drawing technique allowed us to achieve the highest effective draw and hence the highest tensile properties among the drawing techniques examined. In this paper, we report preliminary results on drawing of a commercial UHMW-PE reactor powder by the two-stage drawing technique.

EXPERIMENTAL

The UHMW-PE used was Hercules Hifax 1900 as-received powder ($M_v = \sim 2 \times 10^6$). The powder was compression moulded into a film of ~0.5 mm thick at ~40 kg cm^{-2} and at 130°C, which corresponded to 10°C below the d.s.c. melting peak temperature. Strips of 0.5 mm × 9 mm × 60 mm, cut out from the compacted UHMW-PE powder film, were drawn by a two-stage drawing technique[3,5]. For the first-stage drawing, a strip was sandwiched between split billet halves of high density polyethylene and the assembly coextruded at 110°C through a conical brass die having an entrance angle of 20°. The extrusion draw ratio (*EDR*) of a coextruded film was determined from the deformation of ink marks preimprinted on the surface of a strip. For the second-stage drawing, the extruded films of 5 cm length were drawn by tensile force in a Tensilon tensile tester RTM-100 equipped with an air oven. The drawing was made at constant temperatures of 120–135°C and crosshead speed of 1–20 cm min^{-1}. The tensile modulus and strength of drawn films along the fibre axis were measured at room temperature at a strain rate of 1×10^{-3} s^{-1} and 1×10^{-2} s^{-1}, respectively. The modulus was determined from the slope of the stress–strain curve at low strain (< 0.1 %). The melting characteristics were determined on

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a Seiko-Denshi DSC-10 differential scanning calorimeter at a heating rate of 3°C min^{-1}. The crystallinity of samples was calculated from the heats of fusion assuming 69 cal g^{-1} for a perfect polyethylene crystal. Wide-angle X-ray diffraction patterns were recorded by a flat plate camera with Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Our previous studies[3,5,10] of superdrawing single crystal aggregates of UHMW-polyolefins showed that the first stage coextrusion to a low *EDR* of ~6 markedly improved the drawability and the efficiency of draw for the second-stage tensile drawing. In this work, therefore, a compacted UHMW-PE reactor powder was first coextruded to $EDR=6$ and then further drawn by tensile force at elevated temperatures. Indeed, this first-stage coextrusion was essential to achieve an efficient and high draw when the compacted powder was brittle. Even when the initial sample was brittle, it became ductile on coextrusion at low *EDR*. The drawability of an $EDR=6$ extrudate on the second-stage tensile drawing and the uniformity of the resultant films increased for drawing at higher temperatures. The latter was also increased by drawing at a higher rate. When an extrudate was drawn at a slow cross-head speed (~1 cm min^{-1}), the different portions of the resultant film exhibited different degrees of elongation. Thus, the maximum and uniform *DR* achieved at 135°C and at cross-head speeds of 5–20 cm min^{-1} (initial sample length being 5 cm) was 77.

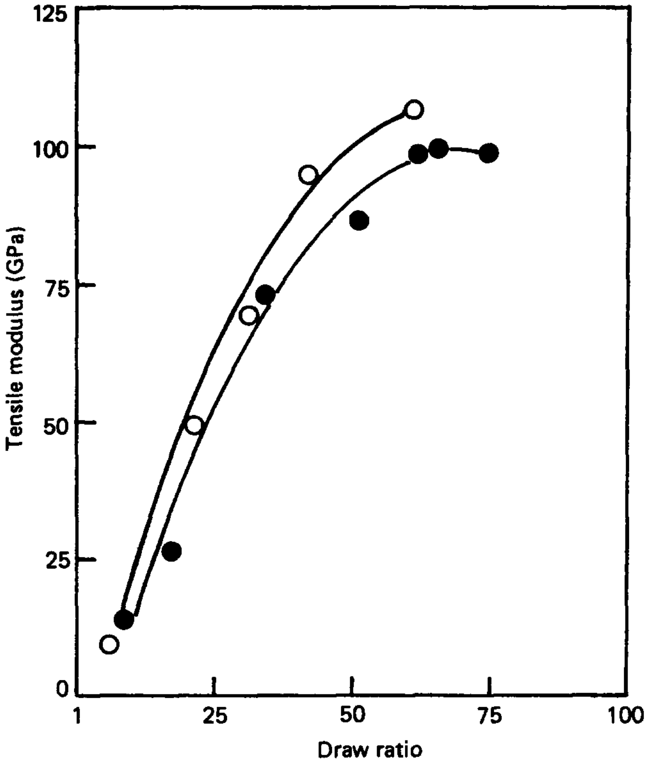

Figure 1 Tensile modulus as a function of *DR* for drawn films of compacted UHMW-PE reactor powder: an initial *EDR* 6 extrudate 5 cm long was drawn at 135°C and at cross-head speeds of: ●, 5 cm min^{-1}; ○, 20 cm min^{-1}

Figure 1 shows tensile modulus as a function of *DR* for doubly drawn films of compacted UHMW-PE powder. The modulus increases rapidly with *DR* up to 100–107 GPa at *DR* 60–77, depending on the draw rates. The efficiency of draw as evaluated by the tensile modulus at a given *DR* is significantly lower for drawing of compacted powder than for drawing of single crystal mats prepared from the same UHMW-PE; i.e. ~100 GPa for the former and 125 GPa for the latter at $DR=60$. This difference is probably caused by differences in the morphology and coherency between the powder particles and the single crystal aggregates, which are important in achieving the efficient draw, as has been shown in previous work on solid-state extrusion of polyethylene single crystal powder[11]. During tensile measurements of highly drawn samples, the fracture commonly developed at a strain of 1–1.7% by a repetitive partial rupture at the edge of sample cramp, resulting in extensive fibrillation. The apparent tensile strength at break, thus observed, was 1.0–1.4 GPa in the *DR* range 35–75, with a less reliable trend with *DR*. These observations suggest that the apparent strengths should be regarded as minimum values for these highly oriented, high modulus and high strength films.

Figure 2 shows wide-angle X-ray diffraction patterns of an original compacted powder (*Figure 2a*), an *EDR* 6 extrudate (*Figure 2b*), and doubly drawn films with *DR* 36 (*Figure 2c*) and 77 (*Figure 2d*). When the incident X-ray beam was directed parallel to the compacted powder film, the (110) and (200) intensity maxima fell on the equator

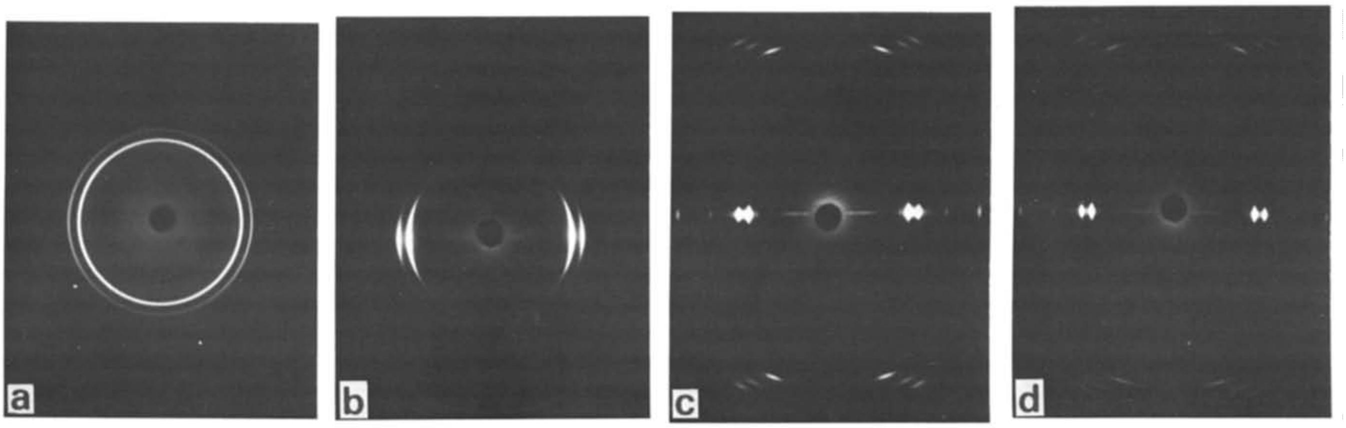

Figure 2 Wide-angle X-ray diffraction patterns of an initial compacted UHMW-PE powder (a), an *EDR* 6 extrudate (b), and doubly drawn films of *DR* 36 (c) and *DR* 77 (d). Photograph (a) was obtained with the incident beam perpendicular to the compression axis. All the drawn films showed uniaxial chain orientation

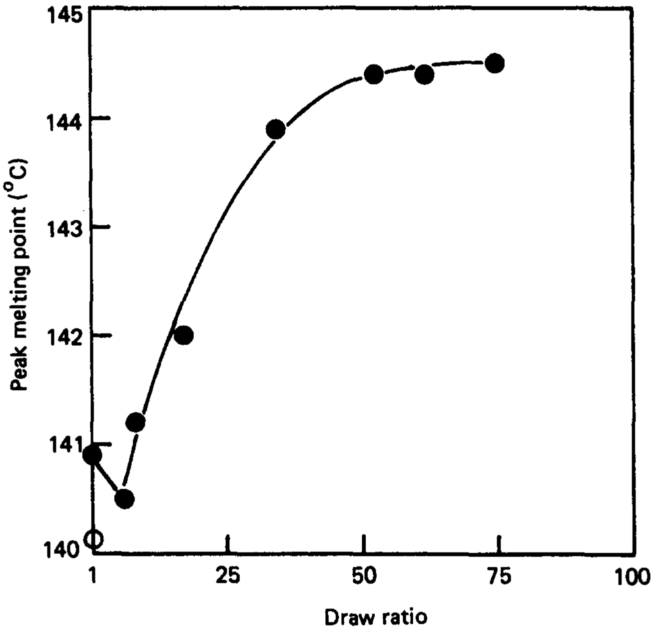

Figure 3 D.s.c. melting peak temperature as a function of *DR*. Heating rate was 3°C min^{-1}. ○, As-received UHMW-PE powder; ●, a compacted powder (*DR* = 1) and drawn samples

(*Figure 2a*). However, when the X-ray was irradiated perpendicular to the film surface, all the reflections showed uniform rings. These X-ray diffraction patterns reveal that the molecular chains are partially oriented in the planes parallel to the surface of the film due to the pressure applied for compaction of the reactor powder into a film. This type of chain orientation is in sharp contrast to that commonly observed on compression of aggregates of single crystal lamellae. When random aggregates of lamellar crystals are compacted, the lamellae orient with the fold surface perpendicular to the applied force, i.e. the chains orient along the force, reflecting the geometry of the crystals. Thus, the different orientation induced by the compression is probably related to the morphological differences between single crystals and the reactor powder. If the latter consists of folded-chain crystal lamellae like the former, the same type of chain orientation would be expected for both materials on compression. These observations, combined with a high melting point of the reactor powder, suggest a highly chain-extended morphology for the nascent UHMW-PE powder. The coextruded film of *EDR* 6 shows a similar degree of chain orientation to that observed for the single crystal mat coextruded at the same *EDR*. The highly drawn films of *DR* 36 and 77 show a similar and high chain orientation. The crystalline chain orientation proceeds rapidly with *DR* and approaches nearly perfect orientation at high *DR*. These changes with *DR* are consistent with the previous results on drawing of melt-crystallized[12,13] and solution-crystallized[13] polyethylene morphologies.

Figures 3 and *4* show d.s.c. melting peak temperature and heat of fusion, respectively, as a function of *DR* for films drawn at 135°C and at a cross-head speed of 5 cm min^{-1}. The melting endotherm of as-received powder exhibited a fairly broad peak at 140.1°C, with a small tail extending down to ~124°C. The crystallinity of the powder calculated from the heat of fusion (47.4 cal g^{-1}) was 69%. On compression moulding the powder at 130°C into a film, the melting behaviour changed significantly: the melting peak slightly increased to 140.9°C and the heat of fusion increased markedly, to 54.8 cal g^{-1} (79% crystallinity) due to significant growth of the low-temperature tail on the melting curve. These observations indicate that a significant amount of less stable components present in the reactor powder reorganized during the compression, even at 130°C, which corresponded to ~10°C below the d.s.c. melting point of the initial powder. On drawing the compacted powder to low *DR* values, in the range 6–8, the low-temperature tail of the endotherms decreased and the melting peak became sharper. However, the peak temperature and heat of fusion decreased at these low *DR* values, with this tendency more prominent for the latter case (*Figure 4*). A similar decrease in crystallinity at low *DR* has been observed and discussed by Chuah and Porter[14], who examined solid-state extrusion of high density polyethylene samples having a range of chain extension produced by crystallization at high temperatures and pressures. On further drawing, the low-temperature tail became less prominent, the melting peak became sharper and shifted to a higher temperature and the heat of fusion increased, as shown in *Figures 3* and *4*. At *DR* > 50, d.s.c. melting behaviour showed no changes with increasing *DR* up to the maximum *DR* of 75. In this *DR* range, the plateau values of melting point and crystallinity were 144.5°C and 85%, respectively. The relationship between tensile modulus and *DR* for the samples drawn at a cross-head speed of 5 cm min^{-1} shown in *Figure 1* is similar to those of melting point and heat of fusion vs. *DR* in *Figures 3* and *4*, respectively. Further improvement of the drawing processes of UHMW-PE reactor powder and the morphological changes during drawing are currently under study.

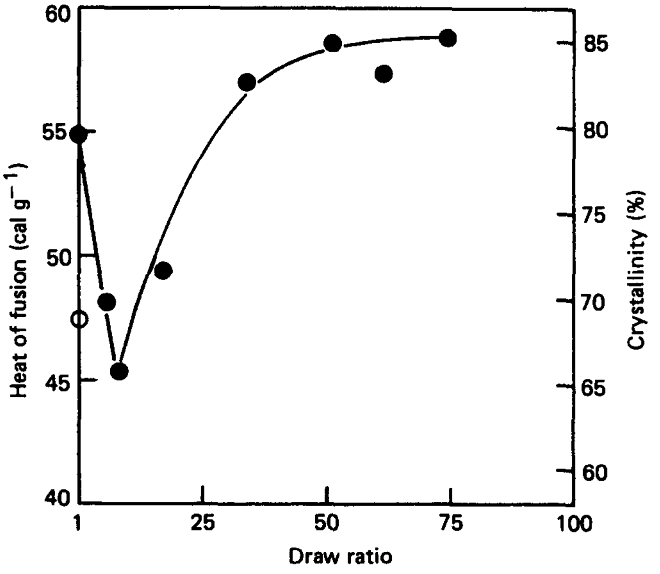

Figure 4 Heat of fusion and the corresponding crystallinity as a function of *DR*. Symbols as in *Figure 3*

CONCLUSION

UHMW-PE reactor powder of a commercial grade has been drawn by a two-stage drawing technique: i.e. solid-state coextrusion of the compacted powder films prepared below the ambient melting point to a low *EDR* of 6, followed by tensile drawing at elevated temperatures of 120–135°C. The drawability for the final-stage tensile drawing and the uniformity of the resultant films were sensitive to the drawing temperatures and rates. The efficiency of draw evaluated by the tensile modulus vs. *DR* was significantly lower than that observed in superdrawing of single crystal mats formed from the same UHMW-PE, indicating that the coherency of crystalline particles and their morphology have an important influence on drawability and efficiency of draw. The maximum *DR* thus achieved was 77, with a corresponding tensile modulus of 100–107 GPa under the experimental conditions employed in this work. As the sample fracture proceeded by a repetitive partial rupture at the edge of cramp, the observed tensile strengths were rather low and in the range 1.0–1.4 GPa at *DR* 35–77. The X-ray diffraction and d.s.c. measurements show the characteristic morphology of UHMW-PE reactor powder in which the molecular chains are highly extended.

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