Die Drawing Technology of High Molecular Weight Polyethylene

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SYNOPSIS

A comprehensive investigation of the die drawing technology of a high molecular weight polyethylene (HMWPE) rod has been carried out. The effect of draw temperature, draw speed, nominal draw ratio, and exit diameter of the dies has been studied. The oriented HMWPE products were characterized mainly by the determination of the three-point bend modulus and the tensile strength. The tensile strength and the modulus of the drawn HMWPE rod could reach 700 MPa and 18 GPa, respectively. In addition, it was found that forced cooling at the die exit was essential when drawing billets with large section areas. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Since Carother and Hill discovered that nylon 6 could be drawn to yield oriented materials of markedly improved mechanical properties,[1] tensile drawing has been used for the production of polymeric fibers and films successfully to enhance their mechanical properties. However, this method has not been used for the production of polymeric rods. Much effort has been devoted to the production of oriented polymeric rods; examples are ram extrusion and hydrostatic extrusion.[2] Ward developed the tensile drawing into a new technique called die drawing, which is a technique that combines the best characteristics of tensile drawing and solid-state extrusion and enables the yield of highly oriented polymer rods and other profiles.[3-5] Die drawing of several polymers, such as high-density linear polyethylene (LPE), polypropylene (PP), polyoxymethylene (POM), poly(vinylidene fluoride) (PVDF), and poly(arylether ketone) (PEEK) has been studied.[3-6] However, few studies have been concerned with the die drawing of high molecular weight polyethylene (HMWPE). This study was concerned with the die drawing of HMWPE and aimed to the manufacture of high strength and high modulus profiles.

2. EXPERIMENTAL

2.1. Billet Preparation

Cylindrical billets for die drawing, with a tapered nose of a semiangle of 15° and a tag of 40 mm length, were prepared by machining from HMWPE rods. These rods were manufactured in Taiwan using the extrusion process. The local supplier could indicate only that the average molecular weight of these rods was about 50×10^4. However, the density, melting point, and melt flow index of this material were determined to be 0.948 g/cm^3, 132–134°C, and 0.20 g/10 min, respectively. The rods were also heated to 130°C (very near to the melting point) and no recovery in the axial and transverse dimensions could be observed. It is known that the recovery of dimensions is normally due to the recoil of the oriented molecules.[7] This implies that the directionality of the rods due to extrusion was not significant. This rod material has a typical spherulite structure, and the average sizes of the spherulites are about 40 μm, with a maximum size of about 60 μm and a minimum of about 15 μm. The spherulites are scattered randomly. These are described in detail in another paper.[8]

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Journal of Applied Polymer Science, Vol. 49, 15–23 (1993)
 CCC 0021-8995/93/010015-09

The billet diameter was chosen to give the required nominal draw ratio, R_N (the ratio of the cross-section area of the billet to that of the die exit). The billets were annealed at 110°C for 10 h before drawing.

2.2. Die Drawing Apparatus

The die drawing apparatus is illustrated in Figure 1. It consists of an aluminum block, a conical die with a 15° semiangle, and two heaters. Two dies, with bore diameter and land length at the die exit of 7.20 × 7.0 mm and 5.00 × 5.0 mm, respectively, were used. The heaters were controlled by two temperature controllers so that the temperatures of the die and the aluminum block could be controlled and adjusted independently. When the die with a 7.20 mm exit was used, in most cases, the temperatures of the aluminum block, the billet, and the conical die were kept equal; however, in some cases, the temperature of the conical die was not equal to the billet temperature.

2.3. Die Drawing Experiment

Die drawing was performed on an Instron 4301 Materials Testing Machine. Before each run, the billet was preheated to the chosen billet temperature in an oven, then placed into the heated aluminum block, so that the tag protruded through the conical die and the grips were attached. After the assembly had attained thermal equilibrium within about 30 min at the chosen temperature, the drawing process was started at low draw speed (i.e., 5 mm/min). When the nose was drawing through the die, the draw ratio increased gradually and reached a specific value when it had been drawn through completely. The process was stopped and the drawn product with the smaller draw ratio was cut off; then the grip was reattached and the process restarted. The draw speed was increased slowly to the required value and the draw load under steady state was recorded. The diameters of the drawn products were measured and were presented as the actual draw ratio, R_A (i.e., the ratio of the cross-section area of the billet to that of the drawn products).

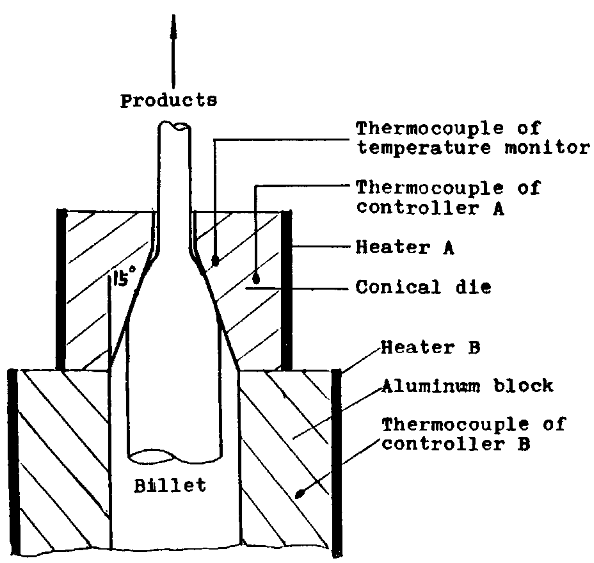

Figure 1 Schematic of the die drawing apparatus.

2.4. Stiffness Measurements

The three-point bend modulus of the drawn HMWPE was tested on an Instron 4301 Materials Testing Machine. With reference to ASTM D790M-86, the support span employed was 102 mm, and the specimen length and the crosshead speed were 130 mm and 2.6 mm/min, respectively. The strain levels were controlled to below 0.2%. It is realized that the end effects would cause a significant underestimate of moduli, in particular, when measuring highly anisotropic material.[9] However, the results obtained still provide some useful information.

2.5. Strength Determination

The tensile strength of the drawn HMWPE were tested on an Instron 4301 Materials Testing Machine at a crosshead speed of 25 mm/min. Specimens for the tensile test were produced by machining the 7 mm-diameter drawn rods to dumbbell shape with about 3 mm diameter and 20 mm length at the machined section. The charpy impact resistance of the 7 mm-diameter drawn HMWPE rods was tested on a CEAST impact testing machine.

3. RESULTS AND DISCUSSION

3.1. Die Drawing Behavior of HMWPE

3.1.1. General Behavior

When the die drawing process was started under selected conditions, the draw load ascended rapidly in the initial stage and attained a maximum value, then descended to a constant value, i.e., to a steady state. This load-extension curve of the drawing process was analogous to the stress–strain curve of PE at room temperature. The drawn HMWPE rods obtained at the steady state were free from faults and their section dimensions were uniform. After drawing, the undrawn opaque HMWPE rod became transparent, and the higher the draw ratio, the higher the transparency. However, when breaking occurred, the broken part still showed some degree of stress whitening. These reflected that the crystal structure of HMWPE changed from larger 10 μm grade spherulites to smaller 100 nm grade microfibrils.[8]

Typical breaking behaviors could be divided into two categories: When the HMWPE billet was drawn at low billet temperature and high R_N, the drawn HMWPE rod was first torn off from the surface and then propagated to the center at the exit of the die, which was caused by the surface fault on the billet. When the material was drawn with a high drawing speed, voids appeared at the core of the rod, and when continuing drawing away from the wall of the exit, the void expanded rapidly and the rod necked, resulting in breaking. The maximum achievable nominal draw ration (R_N, the ratio of the cross-section area of billet to that of the die exit) at various billet temperatures and 25 mm/min speed are listed in Table I.

The diameter of drawn products were slightly smaller than that of the die exit (7.2 mm) and varied from 6.9 to 7.1 mm depending on the draw speed. This indicated that necking had happened to the HMWPE rod during drawing.

Table I Attainable Max R_N Drawn at Various Temperatures

	Billet Temp (°C)				
	85	95	105	115	125
Max R_N (GPa)	9.3	11.1	12.0	13.0	15.1
Max E (GPa)	9.5	13.0	13.3	15.5	13.0

3.1.2. Draw Ratio

Figure 2 shows the effect of billet temperature on the diameter (R_A) of the products drawn at a 25 mm/min speed with a 7.2 mm exit die. It can be seen that the billet temperature has little effect on R_A. For billets with R_N from 4.3 to 12, the R_A vs. billet temperature curves showed little change. The actual draw ratio seems to increase slightly with increasing billet temperature. The effect of draw speed on R_A for a billet with R_N = 13 is shown in Figure 3. It can be observed that the R_A increased with increasing draw speed. When the billet temperature employed was 125°C [Fig. 3(A)], the draw speed could increase up to 100 mm/min and the R_A varied from 13.4 to 15.8. However, when the billet temperature used was 115°C, the draw speed could only attain 35 mm/min and the R_A ranged from 13.4 to 14.4. The R_A's of the products drawn with a 5 mm exit die were almost equal to those drawn with a 7.2 mm exit die [refer to Fig. 3(B)].

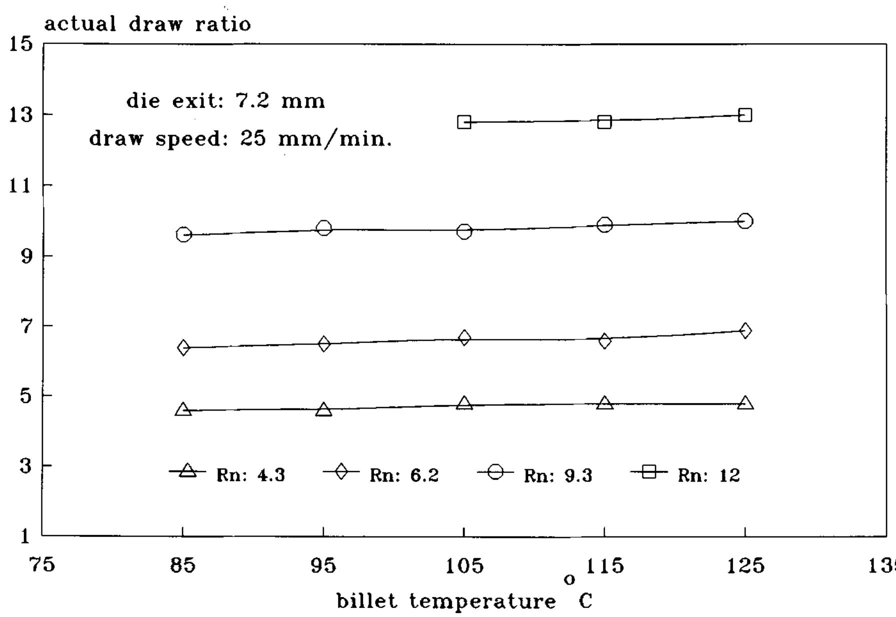

Figure 2 Effect of billet temperature on actual draw ratio.

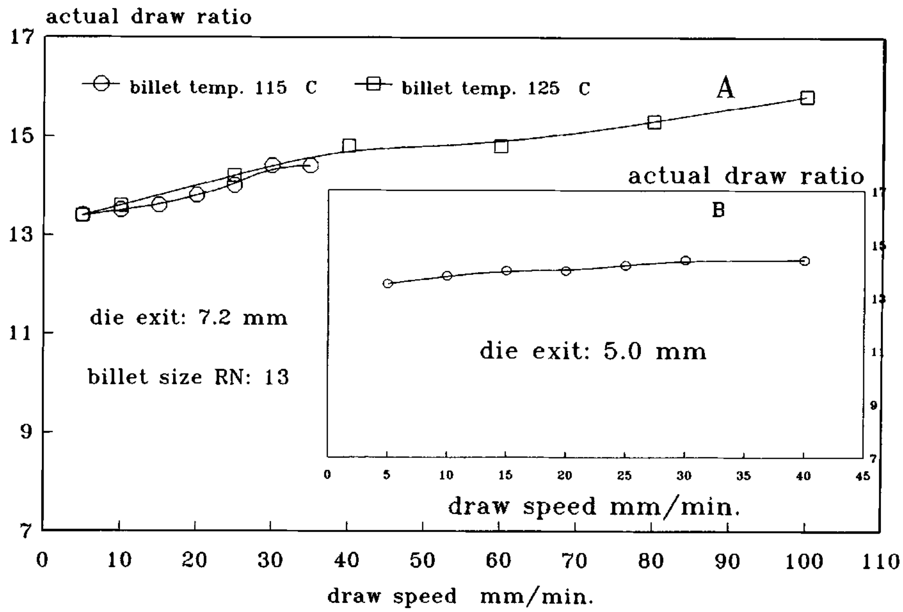

Figure 3 Effect of draw speed on actual draw ratio.

The above results indicate that the billet temperature and draw speed have very little effect on R_A; the main factor affecting the R_A is the original billet dimension (i.e., R_N). To attain a higher R_A, higher R_N billets and lower draw speed should be adopted. This is significantly different from the drawing behavior of LPE. For LPE, the R_A could significantly increase with increasing draw speed.[4] This may be attributed to an increased number of entanglements per chain in melt-crystallized HMWPE, which limited the deformation. But at lower draw speed, the physical entanglement could relax partly and permitted larger deformation.

3.1.3. Draw Load

The variation of steady draw load with billet temperature under various R_N is shown in Figure 4. As

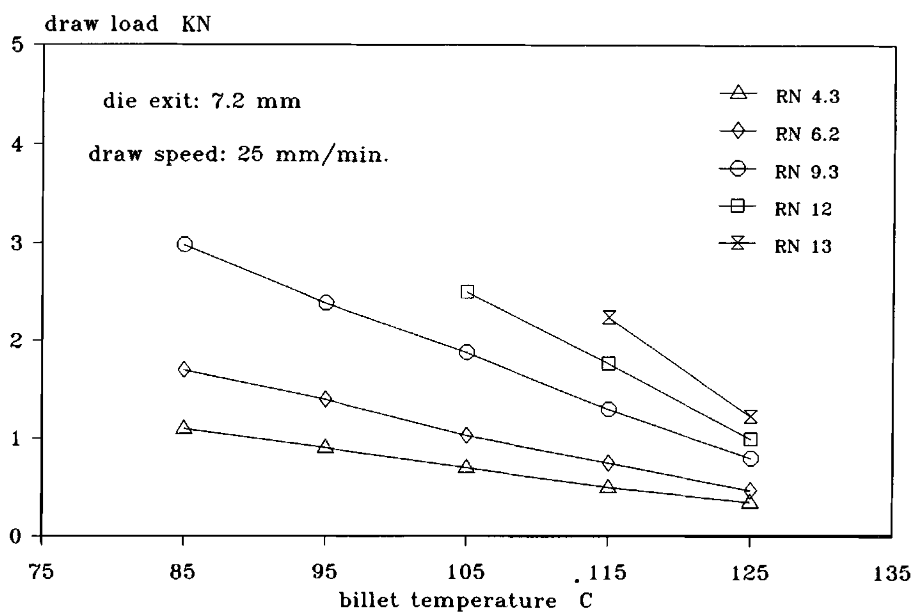

Figure 4 Effect of billet temperature on draw load.

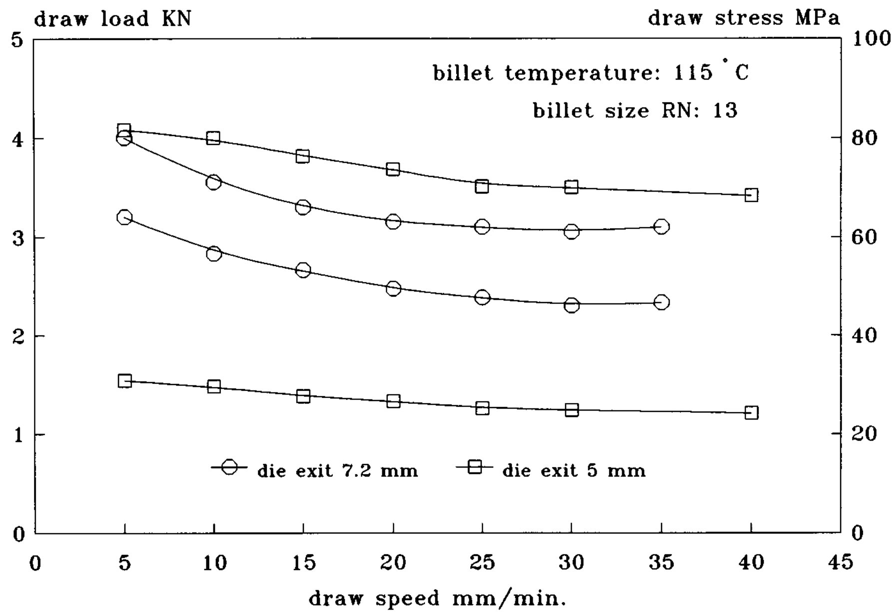

Figure 5 Effect of draw speed on draw load and draw stress.

predicted, the draw load decreased with increasing billet temperature for various R_N billets. It can be observed that when R_N increases the slope of the draw load vs. billet temperature curve becomes steeper.

The variation of draw load and draw stress with draw speed at the so-called steady state for billets with $R_N = 13$ is shown in Figure 5. For both dies with 7.2 and 5 mm die exit, the draw stress at low draw speed (i.e., 5 mm/min) are almost equal. As the draw speed increases, the draw stress decreases but the slope of the draw stress vs. the draw speed curve for the 7.2 mm exit die is larger than that for the 5 mm exit die. This reflects the effect of the built-up heat. HMWPE is not a good heat conductor, the increase in draw speed would accelerate the production of heat during deformation. The heat produced could not be transferred away in time; hence, it would lead to the rise of billet temperature. The consequence of this is the reduction in the flow stress of the HMWPE material. The decrease in the dimension of the die exit would reduce the obstruction to heat transfer; therefore, the effect of draw speed on draw stress is not obvious.

3.2. Mechanical Properties

3.2.1. Stiffness of Drawn HMWPE

The three-point bend modulus of the drawn products was tested on an Instron 4301 Materials Testing Machine. The strain levels were controlled to below 0.2%.

The variation of the three-point bend modulus with billet temperature at various R_N is shown in Figure 6. Within the temperature range of 85–125°C, the moduli of the drawn products increases with increasing R_N. At a billet temperature of 115°C when the R_N increases from 4.3 to 12, the modulus increases from 3 to 13 GPa. However, it can be observed that the general trend for all billets is that when the billet temperature increases the modulus decreases. Within the billet temperature range of 85–105°C, the decrease in modulus is slight, but when the temperature exceeds 105°C, the decrease is significant; i.e., the decrease in billet temperature could increase the modulus of the product especially for high R_N billets. But as the billet temperature decreases, the attainable maximum R_N decreases (refer to Table I), so the attainable highest modulus decreases. Hence, it can be concluded that the optimum billet temperature for the die drawing of HMWPE ranges from 105 to 115°C.

The variation of the moduli of the drawn products with draw speed for a billet with $R_N = 13$ and drawn at a billet temperature of 115°C is shown in Figure 7. It can be observed that when drawn at a 5 mm/min speed, for the products drawn with the die with a 7.2 mm bore, the E is 18.8 GPa, being about 13 times higher than that of undrawn HMWPE. At 10 mm/min draw speed, the modulus has descended to 16.5 GPa; when the speed exceeds 15 mm/min, the

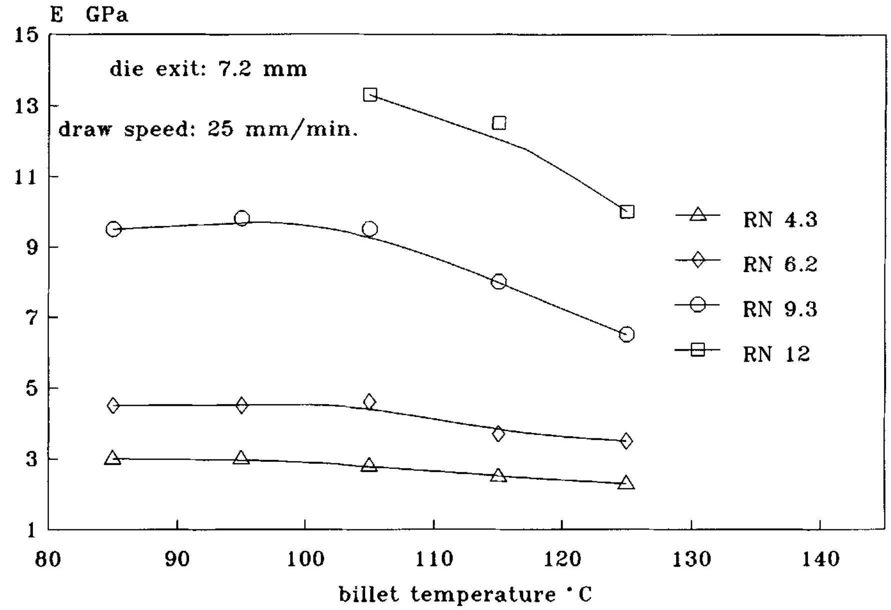

Figure 6 Variation of moduli with temperature at various R_N.

moduli fluctuate around 15.5 GPa. For the products drawn with the 5 mm exit die, the modulus at a 5 mm/min speed was 30 GPa, being much higher than those drawn with the 7.2 mm exit die. The modulus also decreases with the increase of draw speed; when the speed exceeds 30 mm/min, they fluctuate around 20 GPa. The effect of draw speed on the moduli of the drawn HMWPE is significantly related to the built-up heat. This heat increases the temperature of the drawing material and reduces the drawing force; hence, the relaxation of orientated HMWPE speeds up; therefore, the modulus decreases.

To minimize the effect of heat build-up, the temperature of the conical die was controlled below the billet temperature (115°C) during drawing at 25 mm/min speed. Figure 8 shows the effect of die temperature on modulus of the drawn HMWPE where a die with a 7.2 mm exit and a draw speed of 25 mm/min were used. It is clear that the modulus increases with decreasing die temperature. When the

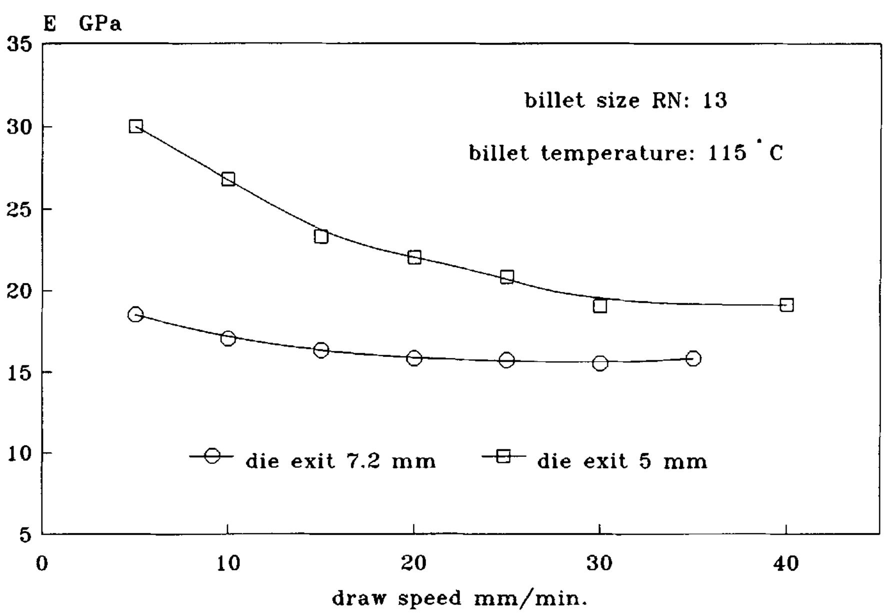

Figure 7 Variation of moduli of drawn HMWPE with draw speed.

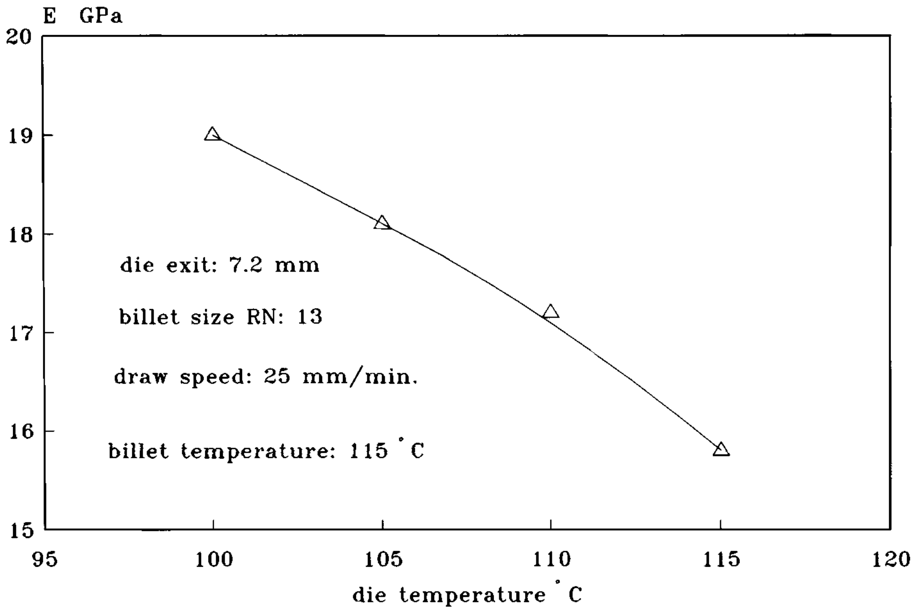

Figure 8 Effect of die temperature on modulus of drawn HMWPE.

die temperature decreases from 115 to 100°C, the modulus of the products increases from 16 to 19 GPa. This indicates that for the die drawing of HMWPE forced cooling at the die exit is necessary, in particular, when drawing large section billets.

3.2.2. Strength of Drawn HMWPE

The drawn HMWPE rods with 7 mm diameter were machined into dumbbell specimens and the tensile strength was tested. The variation of tensile strength of the drawn HMWPE with draw ratio is shown in Figure 9. The tensile strength increases with increasing draw ratio. For the undrawn HMWPE rods, the strength is about 37 MPa. However, for the drawn HMWPE rods with an R_A of 14, the strength increases to 710 MPa, being about 20 times of the undrawn HMWPE rod. The stress–strain curves are shown in Figure 10. The undrawn HMWPE has typical yield necking and cold drawing behaviors.

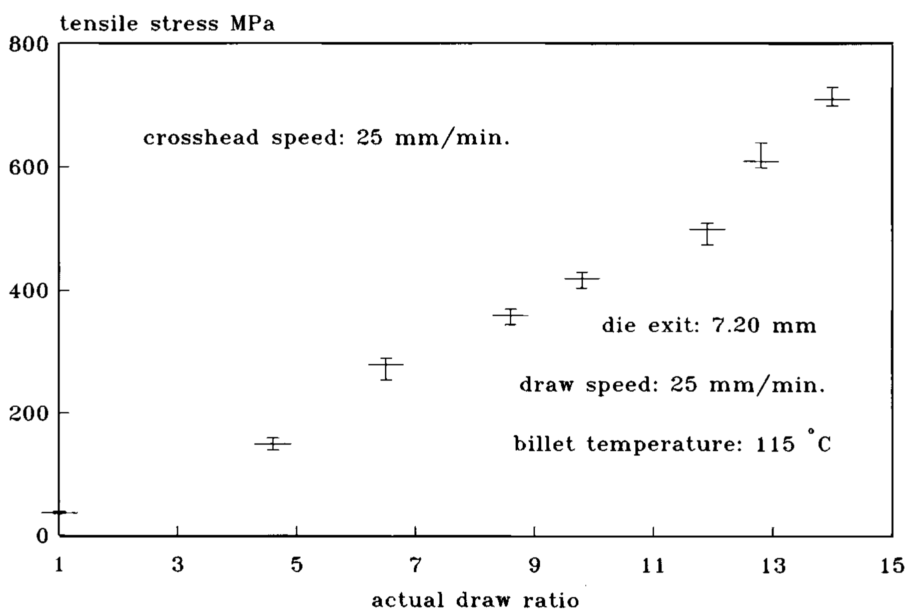

Figure 9 Tensile strength of drawn HMWPE products.

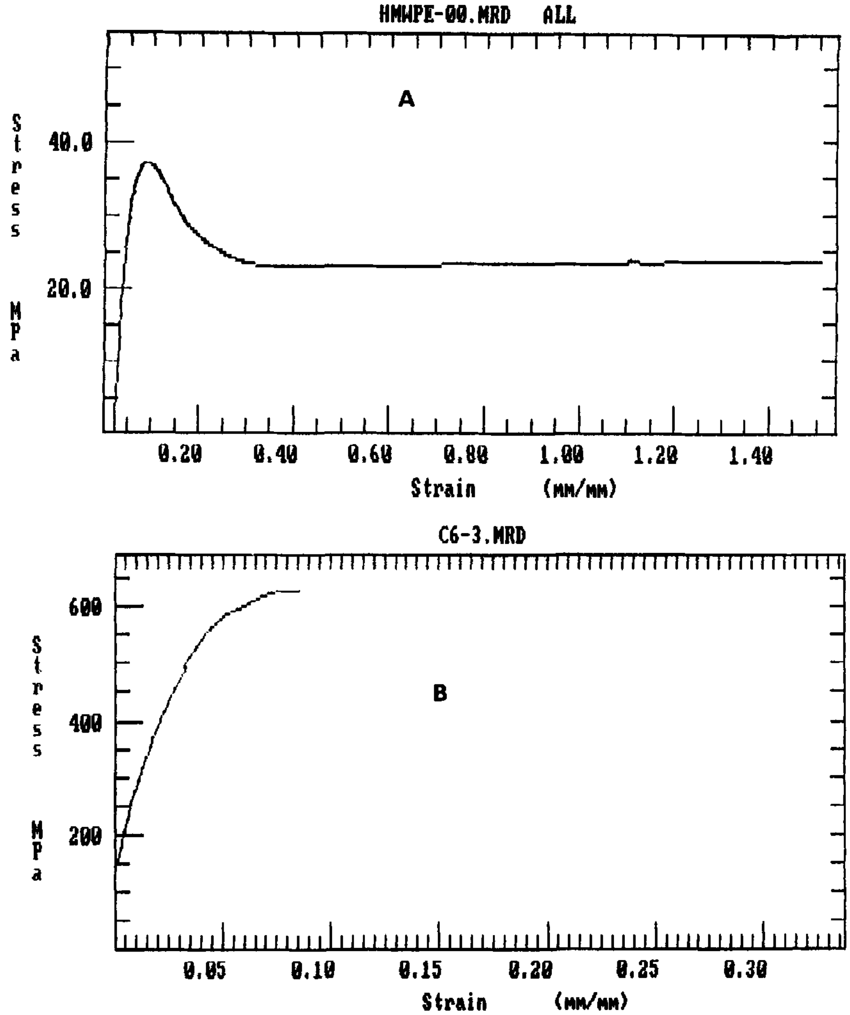

Figure 10 The curves of stress–strain of the drawn HMWPE rod: (A) undrawn HMWPE rod; (B) the drawn HMWPE rod with an actual draw ratio of 12.8.

As the draw ratio increases, cold drawing decreases and strength increases. At draw ratio = 12.8, the yield point disappears; the curve shows quite similar features to those of the stress–strain curve of aluminum.

The impact resistance of the drawn HMWPE rods with 7 mm diameter and modulus of 18 GPa was tested on a CEAST impact tester, which has a maximum impact energy of 25 J. Despite the stiffness of the HMWPE rods being markedly enhanced after being drawn, the drawn HMWPE rods could still stand 25 J impact energy without fracture.

4. CONCLUSION

The die drawing of HMWPE can be performed at low draw speed in the temperature range of 85–125°C. The actual draw ratio of the drawn products is controlled mainly by the original billet dimension. The optimum billet temperature ranges from 105 to 115°C. Multiple-stage controlled temperatures and forced cooling at the die exit are recommended in order to obtain good results; in particular, when drawing billets with large section areas. The drawn HMWPE rod has excellent mechanical properties and the tensile strength and the modulus of the drawn HMWPE rod can reach 700 MPa and 18 GPa, respectively, increasing about 20 times and 12 times compared with the undraw HMWPE rod.

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Received May 13, 1992
Accepted October 6, 1992