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The manufacture of ultra-high modulus polyethylenes by drawing through a conical die

A. G. GIBSON*, I.M. WARD
Department of Physics, University of Leeds, Leeds, UK

Various grades of linear polyethylene have been drawn through a heated conical die at 100° C. It was found that after a suitable start-up procedure, continuous drawing was possible in all cases with a stable neck region extending beyond the die exit. The degree of deformation attainable was found to depend strongly on the draw velocity. Very high deformation ratios could be obtained and the Young's moduli of the die-drawn products were comparable to those of similar products obtained by solid state extrusion and tensile drawing, reaching values as high as 60 GPa. The effects of molecular weight and co-polymerization are substantial, but not exactly analogous to those previously observed in hydrostatic extrusion and tensile drawing. This is probably due to the non-isothermal nature of the final stage of deformation in the case of die drawing.

1. Introduction

In several recent publications [1–8] the tensile drawing and hydrostatic extrusion behaviour of linear polyethylene has been described. It has been shown that the deformation behaviour in both cases is very sensitive to the molecular weight and molecular weight distribution of the polymer in addition to such process variables as temperature and strain rate. In the present paper we will describe the application of another process, die drawing, to the production of high modulus oriented polyethylene. As in the case of tensile drawing and hydrostatic extrusion a wide range of polyethylenes and also a co-polymer have been examined. Die drawing has not previously been applied to the production of highly oriented polymers, but it will be shown to be remarkably successful for polyethylene. Die drawing studies on polypropylene have also recently been undertaken in our laboratories and are the subject of a separate publication [9].

The incentive for die drawing stemmed from our studies of hydrostatic extrusion where it was established that the influence of high pressure was deleterious because of the pressure dependence of the flow stress of the material [8, 10]. A further disadvantage of hydrostatic extrusion through a conical die compared with tensile drawing is that the polymer experiences the highest strain rates at the exit to the die where the plastic strain is greatest. Other work has shown that the strain rate sensitivity of the flow stress increases rapidly with plastic strain [11], hence in extrusion much higher flow stresses are experienced for hydrostatic extrusion compared with tensile drawing where the highest strain rates occur in the neck at comparatively low strains. The combined effects of high strain rates at high strains and the pressure dependence of the flow stress, taken together, account for the limitation of the hydrostatic extrusion process as a means of producing large section high stiffness polyethylenes at commercially acceptable production rates. There was therefore considerable incentive to explore the potential of drawing polymers through a die to combine some of the advantages of tensile drawing with the possibilities of producing large-section material. We will see that

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*Present address: Department of Metallurgy and Materials Science, University of Liverpool, P.O. Box 147, Liverpool, UK.

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this hope was realized, because the plastic deformation occurs not only in the die but also in the region beyond the die exit, and apparently under very favourable conditions of temperature and strain rate giving high modulus products.

2. Mechanical considerations

Die-drawing of metals, i.e. wire-drawing, (Fig. 1a), has been known for a long time. It can easily be shown (see, for instance, [12]), that there is a limit to the degree of deformation which can be imparted in a single pass. For a general strain-hardening material where the tensile flow stress, $\sigma(\epsilon)$ depends on strain (ϵ), the ideal work done per unit volume of material deformed is simply

$$\int_{\epsilon=0}^{\epsilon=\ln R_N} \sigma(\epsilon)\, \mathrm{d}\epsilon$$

where R_N is the deformation ratio. The limiting deformation ratio occurs when the tensile flow stress of the product material is reached, causing it to neck down. The condition for neck formation in die-drawing (neglecting friction and redundant strain effects) is, therefore,

$$\sigma(\epsilon)_{\epsilon=\ln R_N} \leqslant \int_{\epsilon=0}^{\epsilon=\ln R_N} \sigma(\epsilon)\cdot \mathrm{d}\epsilon \qquad (1)$$

This condition is also the condition for the compressive stress between workpiece and die (the die pressure) falling to zero. For a non-work-hardening material ($\sigma(\epsilon) = \text{const.}$) this predicts a limiting R_N value of 2.72. Moreover, the formation of a neck when there is considerable strain hardening at higher strains is not necessarily a catastrophic event. Propagation of a stable neck along a tensile test specimen is common, as is the presence of a stationary neck in continuous drawing of fibres and films. In the latter example the neck is often localized by heat transfer from a heated pin or plate. In die-drawing of polymers we may therefore envisage the situation in Fig. 1b where there are three regions of deformation: (i) conical die flow, (ii) free tensile flow (isothermal); (iii) free tensile flow (non-isothermal).

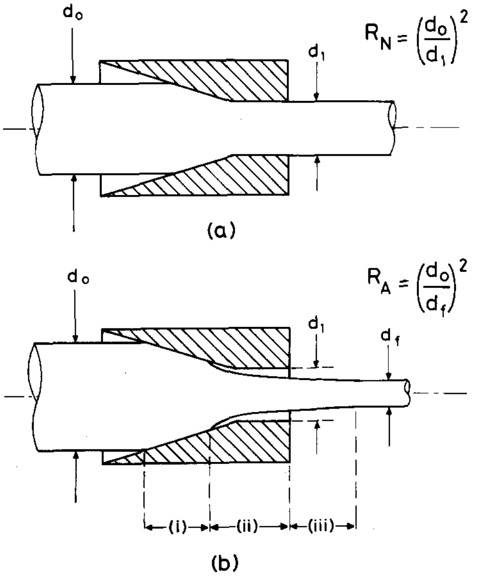

Figure 1 Schematic representation of die-drawing process for (a) non-work-hardening material, (b) polymer material (heated die) with stable neck.

The location of the transition point between zones (i) and (ii) will depend upon condition 1. If the inequality is not met then conical die flow will extend to the end of the die cone. If necking is predicted, then the material will leave the die wall (as shown) at some point within the cone region. The conditions in the tensile flow régime are fairly complex. The portion of the die between the point where the material leaves the die wall and the die exit (zone ii) can be regarded as isothermal, while in region (iii) beyond the die exit, heat will be removed by convection to the surrounding air. The tensile deformation will be gradually "frozen out" at some distance from the die. This point defines the downstream limit of the deformation zone. The non-isothermal régime may be important in two respects: first, it will act as a stabilizing influence on the process since it will tend to counteract the effects of deformational heating within the material (which can induce "thermal" fracture). Secondly, it is known that drawing at lower temperatures is more "effective", that is, it produces a greater improvement in properties than drawing at higher temperatures. The length of the non-isothermal zone will be determined primarily by heat transfer, and will therefore be influenced by the draw velocity and the scale of the process. We will define an "actual" deformation ratio, R_A, as in Fig. 1b in terms of the initial, and final cross-sectional dimensions of the product. (This quantity has also been referred to as λ_{max} in another publication [9].

A major problem in die-drawing of polymers is starting the process. The deformation ratio which can be achieved initially, using an isotropic billet with an unoriented "tag" will of course be limited to 2.72. We have identified three different ways in which the process may be started:

(i) by forming an oriented tag, using some other means: hydrostatic extrusion [13] has been used successfully, or a swaging process could be used as is done in wire-drawing;

(ii) a stepped billet may be used [9], increasing R_N in stages to the desired value;

(iii) a billet may be used with a cone angle which is substantially less than the die angle, allowing R_N to be increased smoothly during start-up.

With methods (ii) and (iii) it is necessary to interrupt the process at some stage to cut off the unoriented "tag". The newly oriented product can then be re-gripped at a point nearer to the die before recommencing drawing. In the present study, method (iii) was used for start-up because it involves minimum wasteage of material.

3. Experimental details

3.1. Materials and billet preparation

Details of the grades of LPE used in this study are shown in Table I. All these polymers were of the Phillips type and were supplied by B.P. Chemicals International Ltd. The three homopolymers were chosen to cover a range of $\bar{M}_w$ values while keeping the ratio $\bar{M}_w/\bar{M}_n$ approximately constant. The co-polymer grade 002 55 (containing ~ 1 to 2 butyl side groups per 1000 carbon atoms) was chosen to investigate the effect of a small degree of co-polymerization. This particular co-polymer was chosen because other studies have shown that it can be used to produce high modulus polyethylenes with superior creep behaviour [14].

TABLE I

Code name	$\bar{M}_w$	$\bar{M}_n$	Melt flow index. g/10 min BS 3412 (1976)
006	135 000	25 500	0.6
H120	220 000	27 800	12*
H020	312 000	33 000	2.2*
002 Co-polymer	155 000	16 900	0.15

*21.6 kg load.

Rods were moulded from granules (except in the case of H020) by an extrusion-moulding technique. This involved filling aluminium tubes with molten polymer and then standing the tubes vertically in an oven at 120° C to crystallize for about 10 h. The high molecular weight H020 material was supplied as a powder and was compression-moulded into rods.

The die used throughout this study was conical, with a semi-angle of 15°. The die-bore and parallel land length were both 4 mm. Billets for die-drawing were machined as in Fig. 2. A variety of values were chosen for d_0, to give a range of R_N values. A billet cone semi-angle of 5° was used for the reasons explained in Section 2, and a 20 mm long tag was provided for initial gripping.

3.2. Experimental procedure

The die-drawing apparatus is shown in Fig. 3. The die was held within a temperature-controlled aluminium block. The block extended far enough upstream to ensure a uniform temperature within the billet material reaching the die. The draw grips were capable of being driven at any constant speed, v_f, within the range 0.4 to 60 cm min^{-1}, the draw load, L, being measured by a load cell mounted behind the die block.

The billet was placed within the heated die block with the isotropic tag protruding through the die and left to achieve thermal equilibrium. To start the process the draw grips were attached to the tag and drawing commenced at a slow speed of 0.5 to 20 cm min^{-1}. The draw load increased quite rapidly and care was needed to ensure that the unoriented part of the tag did not neck down or fracture. During this stage the deformation ratio (and degree of work hardening) of the material leaving the die increased continuously. After about 15 cm (approximately) of material had been drawn the process was halted, the lower deformation ratio material was cut away, and the product re-gripped as close as possible to the die. On restarting, the load increased rapidly to the previous value and then increased more slowly up to a steady value, indicating that all the material

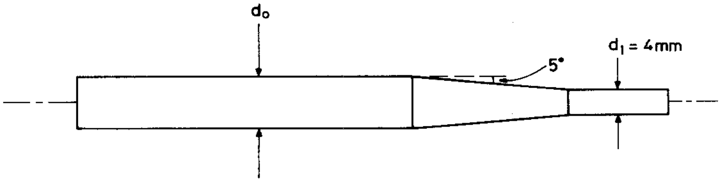

Figure 2 Billet for die-drawing.

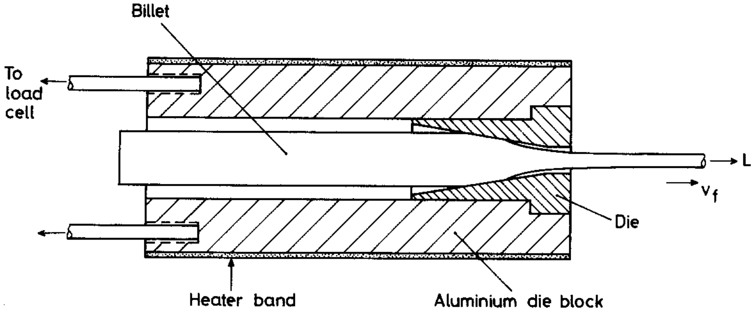

Figure 3 Apparatus for die-drawing.

in the starting "cone" of the billet had been drawn through the die. The process at this stage was considered to have reached steady-state.

As we have already mentioned there is a region of deformation which extends for some distance beyond the die. The length of this post-die deformation region was determined approximately with a micrometer on the moving product and found to vary from about 2 cm in the case of low speed (0.5 cm min^{-1}) operation up to 10 cm or more at a draw speed of 50 cm min^{-1}. Material beyond this point did not vary in diameter, either with time or with distance along the product. We found that diameter measurements made during drawing on material outside the deformation zone agreed very well with measurements made afterwards – indicating a low amount of elastic recovery after deformation. (This particular feature of LPE has been observed previously in hydrostatic extrusion [5], where low degrees of die swell were observed.)

In order to determine the relationship between the dependent parameters, (R_A and L), and v_f a number of experiments were performed at increasing draw speeds, allowing time for steady state drawing to be established at each value of draw speed before taking measurements. When changing draw speed it was found advantageous to do so in a smooth continuous fashion to avoid producing instabilities in the product.

3.3. Product stiffness measurement

The 10 sec Young's modulus at 20° C is accepted as an empirical measure of the structural changes which take place on solid state deformation. Previous studies of both drawing [4] and hydrostatic extrusion [7, 8] have shown that there is a unique relationship between this modulus and the deformation ratio, R_A. This empirical relationship holds fairly well for a wide range of polymer grades and processing conditions. For the present samples a dead-loading flexural (three-point bend) technique was used to determine the 10 sec Young's modulus. The maximum strain in the test was kept to less than 10^{-3}, and precautions were taken to obviate end effects due to anisotropy. (This involved using test samples of high length/diameter ratio [15].)

4. Results

4.1. Die-drawing behaviour

The main dependent variables, R_A and draw load, are plotted against draw velocity in Fig. 4a to d for all the grades of polymer studied. R_A was determined from measurements of product diameter after drawing, although, as mentioned above, these measurements differed very little from diameter measurements taken sufficiently downstream from the die during drawing.

The curves of R_A and draw load for the different grades show a number of similar features. We see that the main effect of increasing the draw velocity was to increase the value of R_A. Even at the lower draw velocities the value of R_A was still substantially higher than R_N, indicating a significant amount of post-die deformation in all cases. At higher draw speeds the slopes of the R_A plots steepen and eventually a limiting velocity was reached, above which the product tended to fail by formation of a localized catastrophic neck. Neck formation was usually accompanied by whitening of the product over a certain region and a drop in draw load. It was sometimes possible to avert failure by lowering the draw speed as soon as these signs were observed. This enabled a maximum draw speed for successful steady state operation to be determined quite accurately for each case. The need for good stability of draw velocity is apparent at the higher values of R_A because of the steepness of the R_A versus v_f plots. The points in Fig. 4 connected by continuous lines correspond to stable steady-state operation with good quality, uniform product.

The effect of increasing R_N (i.e. increasing the diameter of the starting material) is qualitatively

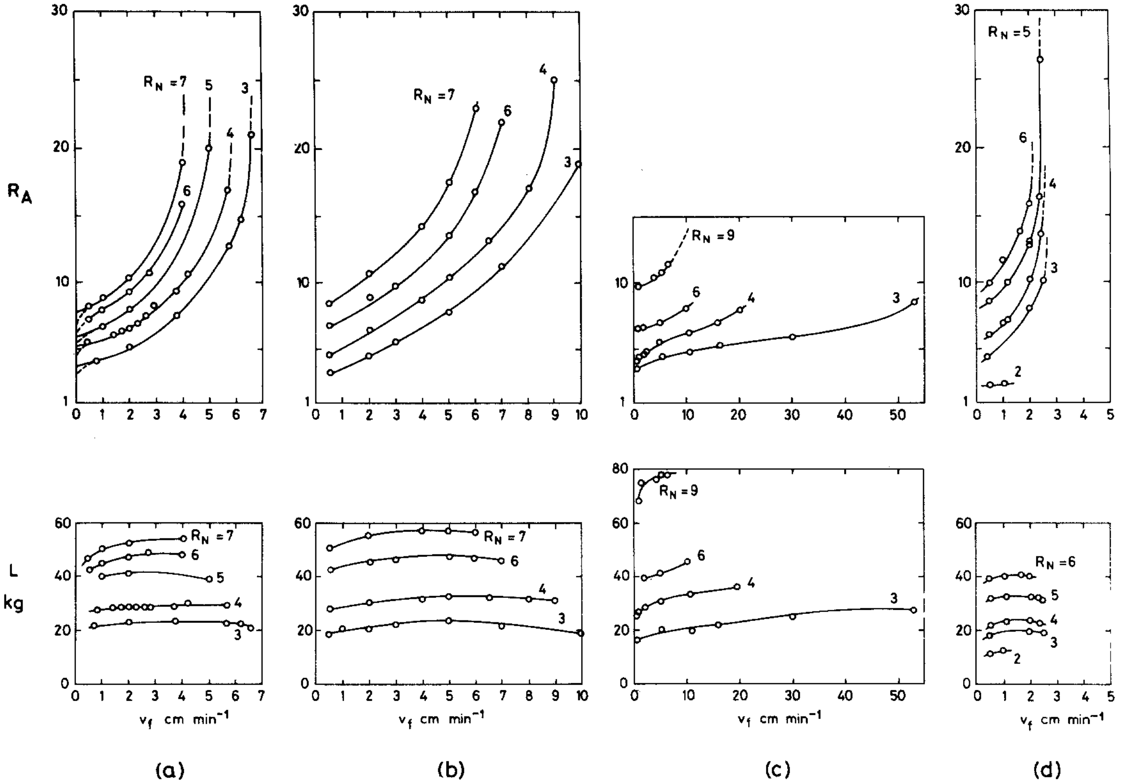

Figure 4 Process variables: deformation ratio (R_A) and draw load (L) as a function of draw velocity (v_f) for different grades of LPE. (a) 006, (b) H120, (c) H020, and (d) 002 co-polymer.

similar to that of increasing draw velocity. It also lowers the value of draw velocity at which the upturn in the R_A curves begins to take place. The use of the term R_N based on the die bore exit diameter in the present context is, to some extent, arbitary when the material leaves the die wall before the die exit. However, the value of R_N does appear to have some influence on the values of R_A at low draw velocities, and the value of d_1 will have a geometrical influence on the length of the isothermal portion (zone ii) of the tensile drawing régime.

The behaviour of draw load with increasing draw velocity is interesting. Although load increased somewhat at low velocities, there was a wide region over which it was almost independent of velocity. Finally, at the highest draw velocities, in the region where the R_A curves are steepest there is a tendency for the draw load to fall slightly with increasing draw speed. In a completely isothermal régime, the latter behaviour would suggest an incipient neck. It seems unlikely that the non-isothermal nature of the post-die régime has a stabilizing effect in a situation where a catastrophic neck might otherwise form.

4.2. Molecular weight effects

The homopolymers used in this investigation can be seen from Fig. 4a to c to follow a trend with increasing molecular weight. This can be seen more clearly in Fig. 5 where the behaviour of the $R_N = 4$ samples is compared between grades. Increasing molecular weight decreases the slope of the R_A versus draw velocity curves, eventually limiting the value of R_A which can be attained with the H020 grade. The value of draw load also increases somewhat with increasing molecular weight.

Perhaps the most surprising result is the effect of the small degree of co-polymerization represented by the 002 grade. The R_A versus draw velocity curve for this material is the steepest of all the materials investigated, although the molecular weight characteristics are quite close to the H120 grade. The draw load is also significantly lower than that of the other grades.

4.3. Stiffness measurements

The 10 sec flexural moduli of the die-drawn products are shown, plotted against R_A in Fig. 6. It can be seen that in the case of the homopoly-

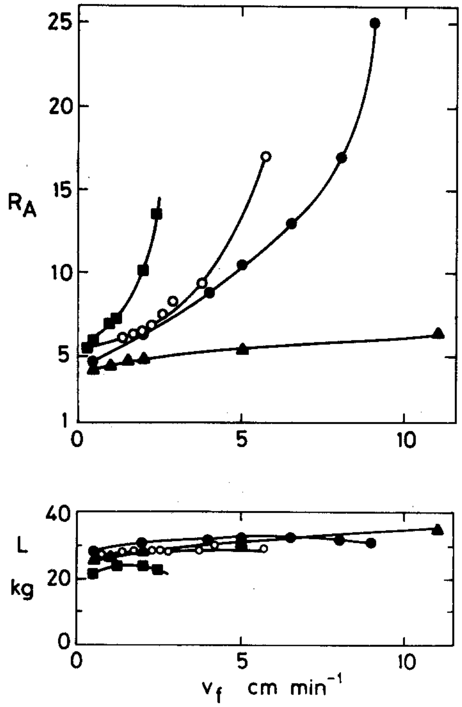

Figure 5 Comparison of behaviour of different polymer grades. Deformation ratio (R_A) and draw load (L) versus draw velocity (v_f) for $R_N = 4$. ○ 006, ● H120. ▲ H020 ■ 002 co-polymer.

mers, the previously observed relationship between modulus and R_A is fairly well borne out. There is, however, a small secondary molecular weight effect, the higher molecular grades having somewhat lower moduli. The behaviour of the 002 co-polymer is again anomalous, giving moduli somewhat higher than those of the homopolymer.

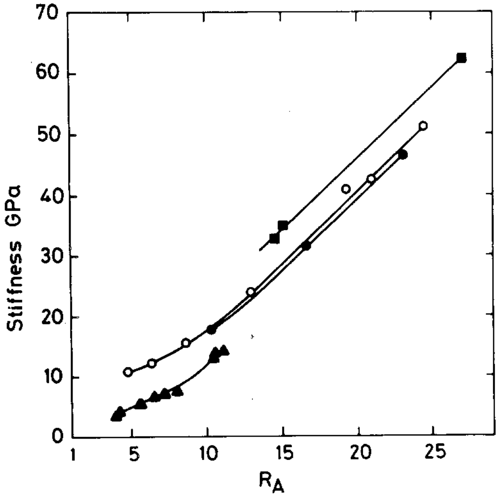

Figure 6 Relationship between 10 sec flexural stiffness and deformation ratio (R_A) for different polymer grades. ○ 006, ● H120, ▲ H020, ■ 002 co-polymer.

5. Discussion

An important aspect of this investigation is that it demonstrates a novel method for the manufacture of thick sections of high modulus polyethylenes. There appear to be a number of immediate advantages over solid-state extrusion processes. In solid state extrusion, for example, the pressure dependence of the flow stress of the material limits the deformation ratio which can be attained [8, 10]. Moreover, a combination of pressure and strain rate effects means that the value of R_A which can be attained decreases with increasing production rate. We have seen that in die drawing, where pressure effects are probably negligible, the reverse is true: R_A actually increases with increasing production rate.

Previous studies of conventional drawing of LPE [8] suggested that high molecular weight polymers were to be preferred in many applications because of their improved creep behaviour. LPE grades in the high molecular weight range (extrusion grades) are also easier to melt process and to mould into large section billets [16] suitable for solid phase forming. Unfortunately, the same materials proved to be difficult to process subsequently: in solid state forming processes, only low values of R_A can be attained [17]. The attainable value of R_A in hydrostatic extrusion [7, 8], for instance, decreases sharply at M.F.I. values below about 5.

Although there is a molecular weight effect in die-drawing, as we see clearly from Figs. 4 and 5, it is still possible to produce fairly large deformation ratios with high molecular weight materials. The highest values of R_A may not yet have been obtained, since the present study was limited to a nominal deformation temperature of 100° C, and there are suggestions [8, 18] that higher temperatures are beneficial for drawing high molecular weight materials.

Fig. 5 shows that although there is a clear correlation between modulus and R_A for each grade of polymer, the unique relationship which was obtained for tensile drawing [1–4] or hydrostatic extrusion [7, 8] is only upheld approximately. The secondary effect due to molecular weight which gives slightly lower moduli for higher $\bar{M}_w$ in the case of the homopolymers was not observed previously. The behaviour of the co-polymer is rather unusual: tensile drawing studies in general given lower moduli for co-polymer grades than for homopolymers, although the former materials give superior creep behaviour.

These results probably reflect the different strain rate and temperature dependence of the flow stress for the different grades of polymer. The differences between the grades which in turn affect the temperatures in the non-isothermal drawing state will therefore be brought out by the differing thermal and strain rate paths followed in the non-isothermal zone (iii). By contrast, in the tensile drawing case, deformation is virtually isothermal so these effects will not appear. The "effectiveness" of the drawing process is known to show different temperature dependence for different grades of material [8], and it may well be that this gives rise to differences in the level of modulus for each material.

The stability of the draw load is interesting. L is determined by the work done by unit volume of material passing through the die-flow zone (zone i) as discussed in Section 2. An increase in draw velocity would tend to increase this work done (and hence increase L) because of the strain rate dependence of the flow stress of the material. However, the criterion for neck formation (Equation 1) suggests that this would be offset by the material leaving the die wall at an earlier point, reducing the work done. Zone (i) therefore acts as a very effective control mechanism for stabilizing the draw load.

If the draw load remains approximately constant then the true stress, σ, experienced by the material in the tensile deformation zone (zone ii) will be a function only of deformation ratio and will be given by

$$\frac{\sigma}{R} = \frac{4L}{\pi d_0^2}, \tag{2}$$

where R is the instantaneous deformation ratio. The quantity $4L/\pi d_0^2$ can be regarded as an "engineering" stress, based upon the cross-section of the starting material. σ/R represents the slope of the Considère construction (see, for instance, Ward [19]) which relates σ to R throughout the tensile deformation zones (ii) and (iii). When σ/R is constant, we infer that the degree of deformation achieved in zone (ii) is determined solely by factors such as the variation of strain rate with strain and temperature and heat transfer.

We have noted that L remains fairly constant over a range of v_f values for a particular set of process conditions. Let us now examine how the quantity $4L/(\pi d_0^2)$ (the Considère line slope, or the "engineering" stress experienced by the deforming material) varies for different values of R_N. This is shown in Fig. 7 for all the grades, values of L having been taken from the "constant" region of the L versus v_f plot for each grade. It is apparent that for each grade of material $4L/(\pi d_0^2)$ remains constant with changing R_N (within the limits of experimental scatter). This is an important result, as it implies that the ratio σ/R at steady state is independent of R_N. In other words, since all samples of a particular grade of material follow the same Considère locus in stress–strain space the main features which we have observed (i.e. the changes which occur in R_A with changing v_f or R_N) must all result from the effects of changing heat transfer conditions in zone (iii). The fact that $4L/(\pi d_0^2)$ remains constant also gives us a means of estimating the steady state value of L for given processing conditions.

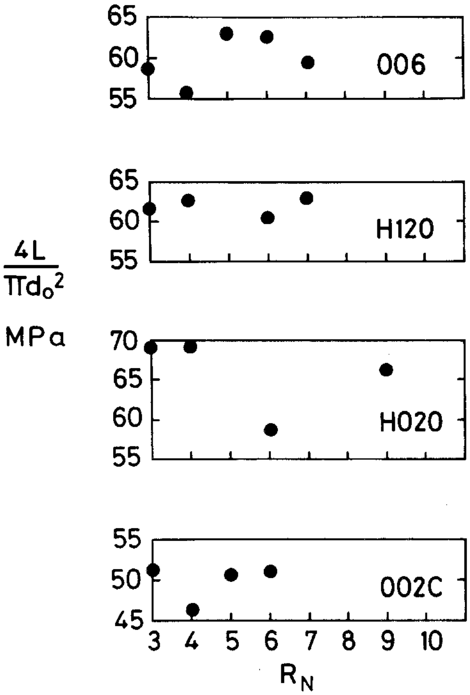

Figure 7 Plots of $4L/(\pi d_0^2)$ (for constant load region) versus R_N for different polymer grades.

It is interesting to note that $4L/(\pi d_0^2)$ increases with increasing molecular weight for the homopolymers, although the behaviour of the copolymer is again anomalous.

6. Conclusions

After adopting a suitable starting procedure, it is possible to continuously die-draw a wide range of grades of LPE to give high modulus products.

In the die-drawing of polymers there are three deformation zones: (i) conical die flow; (ii) free tensile flow (isothermal); (iii) free tensile flow (non-isothermal).

For a given set of conditions the steady state deformation ratio, R_A, increases with draw speed, reaching a limiting value which depends upon the grade of polymer. Increasing the value of R_N (based on billet-die geometry) decreases the draw speed required to attain a particular value of R_A, but does not greatly affect the maximum R_A attainable for a particular material.

The draw load at steady state changes very little with draw speed, the quantity $4L/(\pi d_0^2)$ remaining approximately constant over a range of draw speeds and R_N values for a given grade of material.

The limitations on attainable deformation ratios which were observed at high molecular weights for drawing and solid state extrusion are not as pronounced with die-drawing. Moreover, the deformation ratios achieved with the co-polymer investigated here are much higher than those possible by hydrostatic extrusion. These effects may be associated with the non-isothermal nature of the final stage of deformation, and are probably determined by heat transfer and factors such as the strain, strain rate and temperature dependence of the tensile flow stress.

The empirical relationship between modulus and deformation ratio is again upheld, although there are secondary effects (due to molecular weight and co-polymerization).

Die-drawing can be used to make materials which could previously be produced only by solid state extrusion. However, the die-drawing process has the following advantages over solid state extrusion:

(a) expensive tooling is not required;

(b) R_A increases with increasing production rate;

(c) higher values of R_A can be obtained, particularly in the case of high molecular weight and co-polymer grades;

(d) it is easy to envisage a continuous process.

Acknowledgements

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