Ultra-High Modulus Polyolefins [and Discussion]

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473

Ultra-high modulus polyolefins

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The factors that determine the production of ultra-high modulus linear polyethylene by tensile drawing and hydrostatic extrusion are discussed. In both cases the molecular mass and molecular mass distribution are important, and for low molecular mass polymers the initial crystallization can also play a critical role. The similarities and the differences between the two types of process are indicated.

Following a brief discussion of the structure of these unusual materials, the dynamic mechanical behaviour and other physical properties are considered. It is of especial interest that there is a link between the creep and recovery behaviour and the drawing process.

1. Introduction

In flexible polymers two essentially different approaches have been adopted to the production of ultra-high modulus oriented polymers. The first is the imposition of a very high degree of extensional plastic deformation on a polymer in the solid state. This can be achieved most simply by tensile drawing and has led to the preparation of ultra-high modulus linear polyethylene (Capaccio & Ward 1973), polyoxymethylene (Clark & Scott 1974), and polypropylene (Cansfield *et al.* 1976). Other possible processes are hydrostatic extrusion (Gibson *et al.* 1974) and ram extrusion (Capiati *et al.* 1977). The second approach is the production of an aligned extended molecular structure in a polymer solution or melt followed by, or associated with, crystallization. This approach has been explored in detail by Pennings and coworkers (Zwijnenburg & Pennings 1975) and by Keller and colleagues at Bristol University (Frank *et al.* 1971; Mackley & Keller 1975), and has recently also led to the preparation of ultra-high modulus polyethylene (Zwijnenburg & Pennings 1976). Short strands of ultra-oriented polyethylene have also been produced by the extrusion of a melt under special conditions of temperature and pressure (Southern & Porter 1970).

The discussion in this paper will be largely confined to work carried out at Leeds University on the tensile drawing and hydrostatic extrusion of linear polyethylene. A brief review of the factors influencing the achievement of ultra-high modulus in these two processes will be followed by consideration of the structure and properties of the oriented products.

2. Tensile drawing

In the cold drawing of a typical synthetic fibre such as polyethylene terephthalate (PET), the plastic deformation is localized at a neck and there is a natural draw ratio that governs the thinning from the initial cross-sectional area to the final cross-sectional area. It appears that the magnitude of the natural draw ratio is determined by the limiting extensibility of a molecular network (Allison *et al.* 1966). Although commercial processes often involve hot drawing in the rubbery state where the deformation is homogeneous, the maximum draw ratio that can be tolerated without failure occurring is still limited by the strain-hardening of the network and possibly by associated crystallization. These maximum draw ratios are quite small (*ca.* 5), which

[65]

30-2

is consistent with a tightly tangled molecular network, as indicated by stress–optional measurements (Pinnock & Ward 1966) and spectroscopic studies of molecular orientation (Cunningham *et al.* 1974).

For all drawing processes there is a good empirical correlation between the Young modulus of the drawn material and the molecular orientation and hence the draw ratio, irrespective of the complications due to crystallinity and morphology. It is therefore well known that higher draw ratios imply higher Young moduli even if the absolute magnitudes are still very low compared with those anticipated on theoretical grounds.

Some preliminary studies on the cold drawing of linear polyethylene (LPE) (Andrews & Ward 1970) suggested that the draw ratio was dependent on the molecular mass of the polymer, samples with a low mass average molecular mass $\overline{M}_w$ showing higher draw ratios. Moreover, there appeared to be a unique relationship between the Young modulus and the draw ratio, irrespective of the molecular mass and molecular mass distribution. These results were subsequently confirmed and extended (Capaccio & Ward 1973, 1974), and figure 1 shows the
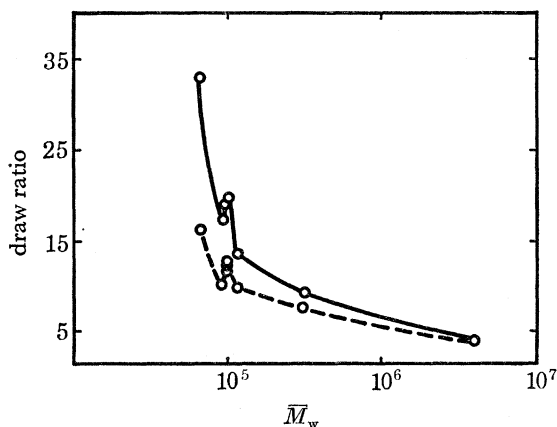

FIGURE 1. Draw ratio plotted against $\overline{M}_w$ for samples drawn at 75 °C for 90 s. ——, Slow cooled; – – –, quenched.

correlation between the draw ratio and $\overline{M}_w$ for LPE samples drawn under more favourable conditions (in particular a draw temperature of 75 °C). Two curves are shown in figure 1, corresponding to different initial thermal treatments, which can be seen to produce dramatic differences in the draw ratio achieved at low $\overline{M}_w$ for fixed time of draw. The two thermal treatments selected are: (1) rapid quenching from the melt where crystallization takes place at high degrees of supercooling, and (2) a more unusual thermal history where the polymer is cooled slowly from the melt to allow crystallization to occur at low degrees of supercooling and then rapidly quenched to room temperature. The difference between the morphologies of the samples is most easily seen from optical micrographs (Capaccio & Ward 1975; Capaccio *et al.* 1976). A typical spherulitic texture develops when crystallization occurs at high supercooling, the lamellae growing out radially from the point of nucleation and branching. Under low viscosity conditions, on the other hand, i.e. low supercooling in low molecular mass samples, branching due to secondary nucleation is less likely and a more uniform lamellar growth occurs, giving rise to regions of homogeneous orientation. The more regular lamellar texture of the latter samples was confirmed by a detailed comparison of small angle X-ray scattering and the low frequency Raman spectrum, combined with measurements of crystal thickness from nitric acid etching

(Capaccio *et al.* 1978). It was concluded that the greater ease of chain unfolding of a more regular lamellar texture and the reduction in the number of tie molecules between lamellae due to the optimum thermal treatment and low $\bar{M}_w$, both contribute to the ease with which high draw ratios can be achieved. There is also another important factor. At the high temperatures required for low supercooling, low molecular mass material will either crystallize very slowly or not at all. Such material could therefore segregate and act as a plasticizer in the drawing process (Capaccio & Ward 1974). The importance of low molecular mass material has been confirmed by Barham & Keller (1977), and it has even been possible to identify its existence as a mobile component in the broad line nuclear magnetic resonance spectrum (Smith *et al.* 1975).

The curves shown in figure 1 do not represent an absolute limit on the draw ratios that can be achieved as a function of $\bar{M}_w$. By increasing the draw time, or by raising the draw temperature,
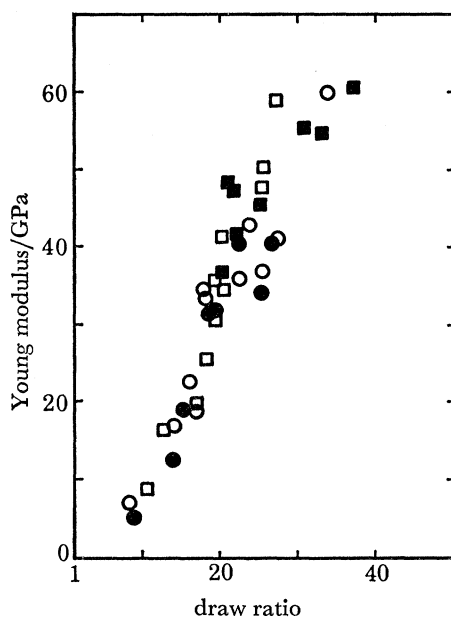

FIGURE 2. Young modulus plotted against draw ratio for samples with $7 \times 10^4 < \bar{M}_w < 10^5$ (■, □) and $\bar{M}_w \approx 3 \times 10^5$ (●, ○). ■, ●, Slow cooled; □, ○, quenched.

LPE with $\bar{M}_w$ up to 800 000 can be drawn to draw ratios of at least 20 with the corresponding increase in Young modulus. For these higher molecular mass materials, the thermal treatment does not affect the drawing behaviour. It has therefore been concluded that the molecular topology and the deformation of a molecular network must be the overriding considerations in limiting the maximum draw ratio and the rate of draw, although for high draw, plastic deformation processes in the crystalline regions must occur. At high $\bar{M}_w$ the drawing behaviour shows several similarities to that of amorphous PET. First, if the draw temperature is raised too greatly, the drawing process becomes ineffective with regard to the production of molecular alignment and hence to the Young modulus. This is similar to the flow drawing of polyesters, where molecular relaxation processes can occur during high temperature drawing, allowing the orientation to decrease. Secondly, at the highest molecular masses, the draw ratio becomes independent of time and a natural draw ratio is again observed.

The LPE studies have refuted the idea that a polymer necessarily has a natural draw ratio dependent only on its chemical constitution and independent of morphology and drawing conditions. Instead it is useful to consider the idea of effective drawing, i.e. drawing which produces molecular alignment and can be assessed in the first instance by the measurement of Young modulus. These studies have established conditions of effective drawing in LPE over a wide range of molecular masses. The corresponding results for the room temperature Young modulus are summarized in figure 2. To a good approximation the Young modulus is a unique function of the draw ratio and very high Young moduli (*ca.* 70 GPa) can be obtained for draw ratios of 30. The guidelines identified in these fundamental studies have been applied to develop commercial processes for fibres and tapes, with draw speeds in the range of 100 m/min or more.

3. HYDROSTATIC EXTRUSION

In parallel with the drawing studies, hydrostatic extrusion was also explored as a method of producing very large solid-phase deformations. It was originally considered that by working in an entirely compressive stress situation, the high strain hardening expected for very high deformation ratios might be overcome by increasing pressure, without any possibility of failure due to tensile fracture. In the event, the limitations on hydrostatic extrusion are more severe than those exhibited in tensile drawing. As will be discussed, these limitations can be very well understood on the basis of an analysis of the mechanics of solid phase extrusion.
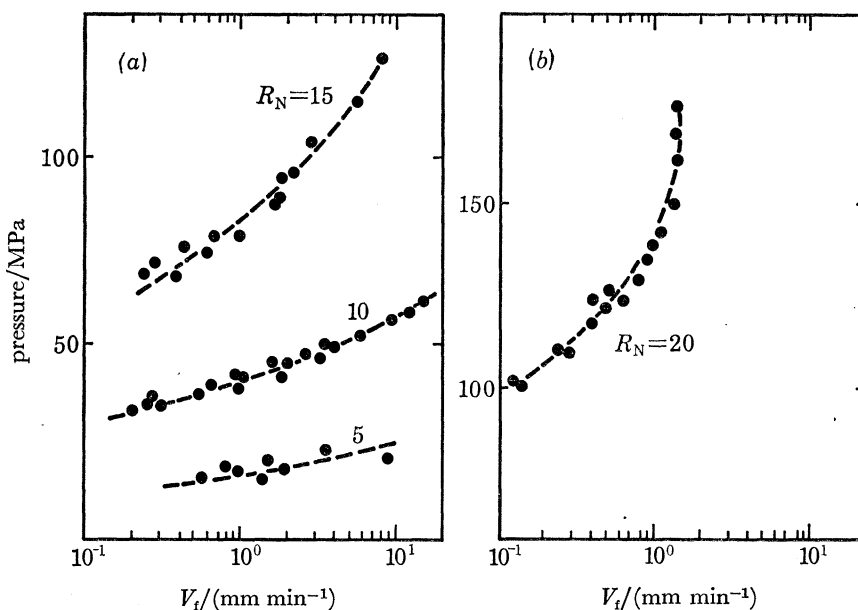

FIGURE 3. Pressure plotted against extrusion velocity V_f for different extrusion ratios R_N.

The hydrostatic extrusion equipment consists basically of a thick walled cylindrical pressure vessel, with a conical die at one end and the entrance for the castor oil pressure-transmitting fluid at the other end. For linear polyethylene, the extrusions were generally performed at 100 °C, and the relation between the extrusion pressure and the extrudate velocity determined for a range of nominal extrusion ratios. The latter is prescribed by the ratio of the cross-sectional area of the polymer billet to that of the die bore at its exit. Typical results for linear polyethylene

are shown in figure 3, from which it can be seen that there is a very rapid upturn in the pressure required to increase the extrudate velocity for high nominal extrusion ratios, leading to a régime where the extrudate velocity cannot be increased by further increases in pressure (Gibson *et al.* 1977). An alternative way of presenting such data, which illustrates the link between tensile drawing and solid state extrusion, is to plot the extrusion pressure as a function of the nominal extrusion ratio for a constant extrudate velocity. This shows that, as in drawing there is a very marked dependence on weight average molecular mass, with the best performance at low $\bar{M}_w$. There is also some dependence on $\bar{M}_n$, materials with a broader molecular mass distribution performing better than those with a narrow distribution.

It is not surprising to find these correlations between tensile drawing and hydrostatic extrusion, because both are solid state deformation processes that are affected by the strain hardening behaviour of the polymer. Recently, an analysis was undertaken of the mechanics of hydrostatic extrusion, which brings out the differences as well as the similarities between the two processes. The Hoffman & Sachs treatment of flow in a conical die, developed for the
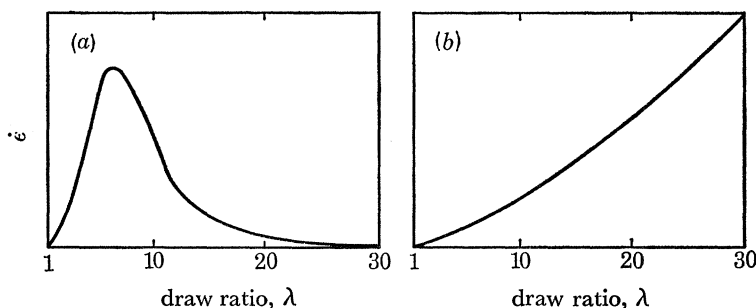

FIGURE 4. Schematic representation of the strain rate ($\dot{\varepsilon}$) fields; (a) tensile drawing, (b) solid state extrusion through a conical die.

extrusion of metals, was adopted (Hoffman & Sachs 1953). To a good approximation the problem is one dimensional and apart from taking into account redundant work at the die entry and exit, it is only necessary to consider the axial equilibrium of thin disk-shaped elements within the die. In principle, knowledge is required of the flow stress criterion for the material and the billet–die friction coefficient. For polymers the problem is complicated because the axial flow stress depends on strain, strain rate and pressure. Studies of the drawing behaviour have shown that the strain-rate dependence of the flow stress greatly increases at higher strains. It can easily be seen that this means that hydrostatic extrusion is at a disadvantage compared with tensile drawing. Figure 4 shows schematically the strain rate fields for the two processes for the case where the total deformation ratio is 30. In tensile drawing, the polymer experiences the highest strain rates at intermediate values of plastic strain. In extrusion, on the other hand, the strain rate increases monotonically from the entry to the exit of the die, and the highest strain rates are experienced at the highest values of plastic strain.

A numerical integration of the modified Hoffman & Sachs equation was carried out for the boundary conditions prescribed in the hydrostatic extrusion process, by calculating the strain rate field for the particular geometry and by using tensile drawing data to determine the strain and strain rate dependence of the flow stress. It was concluded that the rapid increase in slope

of the pressure–extrusion velocity curves at high extrusion velocities can be attributed to a combination of the high strain rate dependence at high plastic strains and the pressure dependence of the flow stress.

The structure and properties of the oriented materials produced by hydrostatic extrusion are very similar to those obtained by tensile drawing (Gibson *et al.* 1974).

4. Structural characterization of drawn polyethylene

Our understanding of the structure of drawn polymers stems from the work of Peterlin, Keller and other workers, who have described the transformation of the original spherulitic morphology to a fibrillar structure. At a molecular level the deformation is considered to be very inhomogeneous and Peterlin (1971) discusses micro-necking processes which lead to the unravelling and alignment of the molecules during drawing. In several respects there are considerable similarities between ultra-high modulus polyethylene and material of lower draw ratio. Scanning electron microscopy shows a fibrillar texture, the fibrils becoming thinner with increasing draw ratio. Quantitative wide angle X-ray diffraction measurements show that almost perfect orientation of the crystalline regions is achieved by a draw ratio of 10. At this draw ratio a clear two point small angle X-ray diffraction pattern is observed, indicating a long period of about 200 Å† which depends on the draw temperature in a manner consistent with previous work (Peterlin & Cornelliussen 1968). The long period observed is independent of draw ratio, but the intensity of the small angle pattern decreases markedly with increasing draw ratio although it is still detectable at the highest draw ratios. This decrease in intensity is consistent with two other observations. First, the broad line nuclear magnetic resonance spectrum of ultra-high modulus materials shows that the non-crystalline material possesses a considerable degree of molecular alignment (Smith *et al.* 1975). Secondly, the average longitudinal dimension of the crystalline regions (the apparent crystal thickness along the *c*-axis) increases with draw ratio from a value of *ca.* 500 Å for highly drawn material (Clements *et al.* 1978).

We believe that a structural model for the ultra-high modulus polyethylene, which is consistent with these observations as well as other properties to be discussed, considers that the lamellar stacks characteristic of the low draw material become increasingly linked by intercrystalline bridges with increasing draw ratio (Gibson *et al.* 1978). In order to establish quantitative links between structure and properties, it has been assumed that the intercrystalline bridges are randomly dispersed across the surfaces of the crystalline regions. The probability of a particular crystalline sequence linking any number of lamellar stacks can then be defined in terms of a single parameter, p, which defines the probability of such a sequence traversing the disordered region to link two adjacent lamellae. The theory is formally identical to the production of the molecular mass distribution produced by a stepwise condensation reaction. The parameter p can be estimated from the integral breadth of the (002) reflexion, and the random model shows that, even for the highest values of crystal continuity estimated ($p \approx 0.4$), the majority of intercrystalline bridges link adjacent lamellae only. This is consistent with the observation that many of these ultra-high modulus drawn LPE samples show melting temperatures as low as 138–139 °C, i.e. below those exhibited by pressure crystallized chain extended material, where the crystal thickness is at least 1000 Å. These results are also in contrast to those for highly oriented LPE produced from solutions or melts where multiple melting peaks have

† $1\text{ Å} = 10^{-1}\text{ nm} = 10^{-10}\text{ m.}$

typically been observed with one component showing a melting point in the region of 145 °C.

At the very highest draw ratios the random intercrystalline bridge model suggests a structure which could be equally well envisaged as a continuous crystal containing periodic regions of disorder. This is consistent with the very low gas permeability of those materials and their very high resistance to attack by chemical reagents such as fuming nitric acid and xylene.

5. MECHANICAL BEHAVIOUR

Although the room temperature isochronal creep moduli shown in figure 2 indicate the efficiency of the drawing as a means of increasing the Young modulus, a more quantitative basis for assessing these materials is obtained from the measurement of the dynamic mechanical behaviour (Smith *et al.* 1975). The low temperature dynamic modulus reaches a value of 170 GPa, which is about two-thirds of the value suggested by several theoretical estimates (Frank 1970) and crystal strain measurements (Sakurada *et al.* 1962). It can also be seen that even at the highest draw ratios, these materials show pronounced visco-elastic behaviour with both the α and γ relaxations being clearly evident (figure 5).
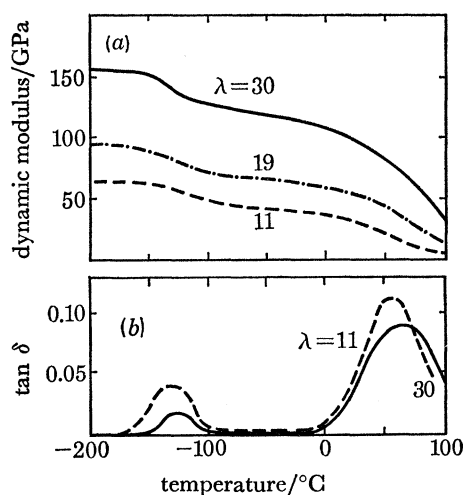

FIGURE 5. (*a*) Dynamic modulus and (*b*) tan δ plotted against temperature for drawn LPE at indicated draw ratio (λ).

The dynamic modulus curves show two distinct plateau regions on either side of the γ–relaxation where the behaviour is elastic to a good approximation. It has been found that the higher temperature (-50 °C) plateau modulus can be correlated with the degree of crystal continuity estimated from the wide-angle X-ray diffraction data. A simple representation of the behaviour can be given in terms of a Takayanagi-Type mechanical model (Takayanagi 1965), where crystalline sequences that link two or more lamellae are regarded as in parallel with the remaining lamellar material and the non-crystalline material which are in series. On the random intercrystalline bridge model described above the volume fraction of the continuous crystal phase is given by $V_f = \chi p (2-p)$, where χ is the volume fraction of crystalline material, and the modulus of the sample is

$$E = E_c \chi p (2-p) + E_a \frac{\{(1-\chi) + \chi(1-p)^2\}^2}{(1-\chi) + \chi(1-p)^2 E_a/E_c},$$

(1)

[71]

where E_c and E_a are the extensional moduli of the crystalline and non-crystalline material respectively.

In the $-50\ °C$ plateau region above the γ–relaxation $E_a \ll E_c$ and equation (1) reduces to $E = E_c \chi p\,(2-p)$. It has been shown that experimental results for both drawn and extruded materials are in good agreement with this.

In terms of the mechanical model the rise in modulus as the temperature is lowered through the γ–relaxation is attributed to the stiffening of the non-crystalline material. The increases in modulus shown by these materials are considerable, and this is consistent with appreciable degrees of molecular orientation in the non-crystalline material. Although the fall in modulus at high temperature can be represented in the model by a crystalline relaxation process affecting the magnitude of E_c, it is more instructive physically to consider that this relaxation process affects the transfer of stress between the lamellae by the intercrystalline bridges. The situation is then formally analogous to an aligned short fibre composite where the fibres are the crystalline sequences which link two or more lamellae, and the matrix is a mixture of lamellar crystals and the non-crystalline material. Equation (1) becomes

$$E = E_c\,\chi p(2-p)\,\phi' + E_a\,\frac{\{(1-\chi)+\chi(1-p)^2\}^2}{(1-\chi)+\chi(1-p)^2\,E_a/E_c}, \qquad (2)$$

where we have introduced an average temperature dependent shear lag factor ϕ' to represent the loss of stiffness due to the α relaxation. Barham & Arridge (1977) have also advocated the phenomenology of a fibre composite model to explain the mechanical behaviour of these materials. Their physical interpretation of the model is, however, somewhat different. They propose that the ultra-oriented material consists of needle-like crystals embedded in a matrix of remaining material. These crystals have retained their identity during the drawing process and the increase in stiffness arises owing to their change in aspect ratio, which increases the shear lag factor. In the model proposed here the proportion of 'fibre phase' changes during deformation and the shear lag factor is introduced to explain the fall in modulus at high temperatures. Valuable supporting evidence for the interpretation of the mechanical stiffness in terms of equations (1) and (2) has come from X-ray determination of the average crystal strain as a function of temperature, for samples of different draw ratio and molecular mass (Clements *et al.* 1978).

6. OTHER PHYSICAL PROPERTIES

A key factor in the increase of stiffness is the increasing degree of crystal continuity. This is directly reflected in the longitudinal coefficient of expansion of the ultra-drawn polyethylene, which is indistinguishable from that determined for the crystal over the temperature range $-180\ °C$ to $+100\ °C$. The thermal conductivity of these materials has also been measured in extruded samples in the directions parallel ($K_\parallel$) and perpendicular to the extrusion direction (Gibson *et al.* 1977). At $-173\ °C$, $K_\parallel$ has a value comparable to that of stainless steel, and shows a linear correlation with the $-50\ °C$ plateau modulus. It is therefore not surprising that the thermal conductivity data can be most simply understood in terms of the thermal analogue of the Takayanagi model. At high temperatures $K_\parallel$ remains high, but with the decrease in the phonon mean free path, considerable scattering occurs because there are comparatively few long crystal sequences.

The high degree of crystal continuity is also reflected in the low shrinkage of the ultra-high modulus polyethylenes until temperatures comparatively close to the melting point. Very high

shrinkage stresses are observed at temperatures of 100 °C or thereabouts, which is an indication of the comparatively high molecular orientation of the non-crystalline regions, as mentioned previously in connection with other observations.

Because of the possible applications of ultra-high modulus polyethylene in the reinforcement of brittle matrices, the creep and recovery behaviour has been examined in some detail (Wilding & Ward 1978). A very marked decrease in creep and creep rate is observed when the molecular mass of the polymer is increased, for samples of similar draw ratio and Young modulus. It can be shown that the creep is the sum of two components: a linear recoverable component, which can be modelled to a good approximation by a simple linear solid representation, and a nonlinear non-recoverable component which can be represented by a thermally activated rate process, and which is markedly affected by polymer molecular mass. In particular, although low molecular mass polymer fits an Eyring rate process down to the lowest stress levels, for high molecular mass polymer there is a threshold stress below which the non-recoverable creep is negligibly small. The creep results are of technological importance because they show the advantage of high molecular mass polymer for some applications. They are also of interest in establishing a link between the creep behaviour of the drawn polymer and the drawing process. The activation values obtained for the non-recoverable creep component are similar to those obtained from true stress–strain–strain rate tensile drawing curves. For Rigidex 50 grade polymer where a direct comparison has been made, in both cases the activation volume is comparatively small (*ca.* 50 Å³) and can be tentatively identified with a localized deformation process such as the pulling out of a chain fold.

REFERENCES (Ward)

Allison, S. W., Pinnock, P. R. & Ward, I. M. 1966 *Polymer* **7**, 66–69.
Andrews, J. M. & Ward, I. M. 1970 *J. Mater. Sci.* **5**, 411–417.
Barham, P. J. & Arridge, R. G. C. 1977 *J. Polym. Sci., Polym. Phys. Edn* **15**, 1177–1188.
Barham, P. J. & Keller, A. 1976 *J. Mater. Sci.* **11**, 27–35.
Cansfield, D. L. M., Capaccio, G. & Ward, I. M. 1976 *Polym. Engng Sci.* **16**, 721–724.
Capaccio, G., Crompton, T. A. & Ward, I. M. 1976 *J. Polym. Sci., Polym. Phys. Edn* **14**, 1641–1658.
Capaccio, G. & Ward, I. M. 1973 *Nature, phys. Sci.* **243**, 143.
Capaccio, G. & Ward, I. M. 1974 *Polymer* **15**, 223–238.
Capaccio, G. & Ward, I. M. 1975 *Polymer* **16**, 239–243.
Capaccio, G., Ward, I. M., Wilding, M. A. & Longman, G. W. 1978 *J. macromolec. Sci.* B **5**, 381–407.
Capiati, N., Kojima, S., Perkins, W. & Porter, R. S. 1977 *J. Mater. Sci.* **12**, 334–340.
Clark, E. S. & Scott, L. S. 1974 *Polym. Engng Sci.* **15**, 682–686.
Clements, J., Jakeways, R. & Ward, I. M. 1978 *Polymer* **19**, 639–644.
Cunningham, A., Ward, I. M., Willis, H. A. & Zichy, V. I. 1974 *Polymer* **15**, 749–756.
Frank, F. C. 1970 *Proc. R. Soc. Lond.* A **319**, 127–136.
Frank, F. C., Keller, A. & Mackley, M. R. 1971 *Polymer* **12**, 468–473.
Gibson, A. G., Coates, P. D. & Ward, I. M. 1977 *Proceedings of the International Conference on Polymer Processing* Massachusetts Institute of Technology.
Gibson, A. G., Davies, G. R. & Ward, I. M. 1978 *Polymer* **19**, 683–693.
Gibson, A. G., Greig, D., Sahota, M., Ward, I. M. & Choy, C. L. 1977 *J. Polym. Sci., Polym. Lett. Edn* **15**, 183–192.
Gibson, A. G., Ward, I. M., Cole, B. N. & Parsons, B. 1974 *J. Mater. Sci.* **9**, 1193–1196.
Hoffman, D. & Sachs, G. 1953 *Introduction to the theory of plasticity for engineers*. New York: McGraw Hill.
Mackley, M. R. & Keller, A. 1975 *Phil. Trans. R. Soc. Lond.* A **278**, 29–66.
Peterlin, A. 1971 *J. Mater. Sci.* **6**, 490–508.
Peterlin, A. & Corneliussen, R. 1968 *J. Polym. Sci.* A 2, **6**, 1273–1282.
Pinnock, P. R. & Ward, I. M. 1966 *Trans. Faraday Soc.* **72**, 1308–1320.
Sakurada, I., Nukishina, Y. & Ito, T. 1962 *J. Polym. Sci.* **57**, 651–660.
Smith, J. B., Davies, G. R., Capaccio, G. & Ward, I. M. 1975 *J. Polym. Sci., Polym. Phys. Edn* **13**, 2331–2343.
Smith, J. B., Manuel, A. J. & Ward, I. M. 1975 *Polymer* **16**, 57–65.

Southern, J. H. & Porter, R. S. 1970 *J. Appl. Polym. Sci.* **14**, 2305–2317.
Takayanagi, M. 1965 *Proceedings of the Fourth International Congress of Rheology* part 1, pp. 161–187. New York: Interscience.
Wilding, M. A. & Ward, I. M. 1978 *Polymer* **19**,969–976.
Zwijnenburg, A. & Pennings, A. J. 1975 *Colloid Polym. Sci.* **253**, 452–461.
Zwijnenburg, A. & Pennings, A. J. 1976 *J. Polym. Sci., Polym. Lett. Edn* **14**, 339–346.

Discussion

G. MANFRE (*Centro Ricerche Fiat, Orbassano, (TO) Italy*). The comparison Dr Ward has shown between the cold drawn process through a die and the simple extrusion method cannot be completely satisfactory. In fact in the cold drawn process, and especially in the hydrostatic extension, a compression, normal to the die axis, is present simultaneously to the extrusion. I should like to know Dr Ward's opinion on this point.

I. M. WARD. The comparison is between tensile drawing and hydrostatic extrusion through a conical die. In our analysis of the extrusion process we set up a force balance which includes the effect of the component due to the normal stress. This is similar to the classical treatment of Hoffman & Sachs 1953.