Study of the production of ultra-high modulus polyoxymethylene by tensile drawing at high temperatures

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The tensile drawing behaviour of polyoxymethylene has been studied, with particular reference to the production of ultra-high modulus oriented material. The influence of molecular weight and draw temperature, and the comparative effectiveness of single-stage and two-stage drawing processes have also been examined. In addition to the molecular weight range it appears that both draw temperature and drawing rate must be specified within very narrow limits, if ultra-high modulus material is to be produced. It is tentatively suggested that this is because effective high draw requires a suitable coincidence of rate processes involving both the crystalline and non-crystalline regions of the polymer.

INTRODUCTION

In several recent publications from this laboratory[1,2] it has been shown that it is possible to produce ultra-highly oriented polyolefins (linear polyethylene, LPE, and polypropylene, PP) under carefully controlled drawing conditions, provided that the molecular weight and thermal treatment of the initial polymer are also optimized. Another polymer for which we have also been successful in producing ultra-high modulus drawn products is polyoxymethylene (POM). Although results for this polymer were described in a provisional patent application[3], our scientific publications have so far been confined to LPE and PP. Particularly in view of the reported studies of Clark and Scott[4] which discuss the preparation of ultra-oriented POM fibres by two-stage drawing, it is clearly of interest to consider whether the guidelines which we have suggested for drawing of LPE and PP are relevant in POM. In this paper we therefore describe an investigation which has examined (a) the influence of molecular weight and draw temperature on the drawing behaviour and (b) the comparative effectiveness of single-stage and two-stage drawing processes.

We have undertaken measurements of initial modulus to monitor the effectiveness of the drawing process. Melting point data and limited structural measurements are also reported.

EXPERIMENTAL

Sample preparation

The materials used were three grades of commercially available POM, Delrin 100, 500 and 8010 as supplied by du Pont de Nemours, Delaware, USA. The molecular weight characteristics of the different grades are given in *Table 1*. The procedures used to obtain these molecular weight values are described in detail by Koch and Lindvig[5].

For the majority of the drawing experiments sheets of thickness 0.5–0.7 mm were obtained by compression moulding pellets of polymer at 200°C between polished copper plates. Some sheets were immediately quenched in cold water on removal from the press (200/W) whilst others were allowed to slow cool down to room temperature (200/SC).

Dumb-bell samples with gauge dimensions 20 x 4.75 mm were cut from these sheets and drawn on an Instron Tensile Testing machine at temperatures varying between 98°–165°C at crosshead speeds of 10 or 100 mm/min. The draw ratio was measured from 0.2 mm diameter marks on the surface of the undrawn samples spaced at intervals of 1 mm. Homogeneous draw was normally obtained over 60–80% of the drawn segment.

Mechanical measurements

To maintain continuity with the previous investigations on LPE and PP, the Young's moduli of the drawn samples were measured by a dead loading creep experiment[6]. The values quoted refer to the secant modulus calculated from the 10 sec isochronal stress–strain curves at a strain of 10^{-3}. The cross-sectional areas of the samples were determined by weighing a length of sample in a microbalance and determining the sample densities in a toluene/carbon tetrachloride density gradient column. Up to draw ratio ~12 the densities were typically in the range of 1.41 g/cm^3. For the higher draw ratio samples ($\lambda > 12$) voiding occurred and the densities could fall as low as 1.265 g/cm^3. We were not able to establish any systematic correlation between the occurrence of voiding and processing conditions – hence the necessity to make density measurements in all cases. The accuracy of individual modulus measurements is estimated as ~±5%. As all the conclusions will be based on comparing a series of modulus measurements (for example as a function of draw

Table 1 Molecular weight characteristcs for POM grades

Grade	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
100	60 000	≃ 2
500	45 000	≃ 2
8010	30 000	≃ 2

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Table 2 Summary of draw temperature ranges

Polymer grade	Thermal treatment	Drawing behaviour
100	Slow cooled	Draw above 160° C only
	Quenched	Draw above 142° C only
500 8010	Slow cooled	Would not draw in temperature range 98° – 165° C
500 8010	Quenched	Draw in temperature range 98° – 168° C

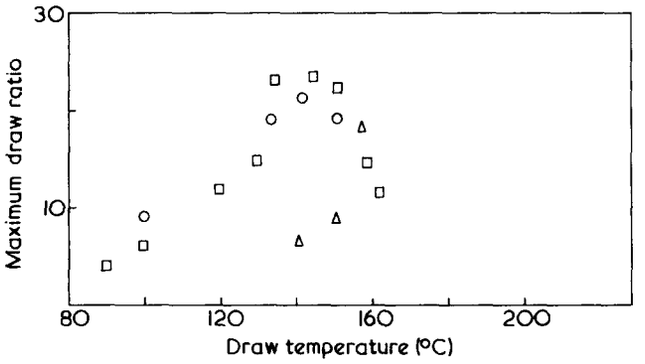

Figure 1 Maximum draw ratio (λ) vs. draw temperature. □, Delrin 500 (200/W); ○, Delrin 8010 (200/W); △, Delrin 100 (200/W)

ratio for drawing under different conditions) this order of accuracy is very adequate for the purpose of the present study.

Differential scanning calorimetry (d.s.c.)

The melting behaviour of drawn samples was examined using a Perkin–Elmer DSC-2. The d.s.c. curves were obtained at a standard heating rate of 10°C/min, and melting points determined using the indium leading edge method. The equipment was calibrated with standard indium and tin samples.

X-ray measurements

Measurements of the crystallite orientation and thickness were made with a Siemens K4 recording X-ray diffractometer using the (009) reflection.

RESULTS

Drawing behaviour

Single-stage drawing. The possibility of successful drawing depended on both molecular weight and initial thermal treatment. A summary of the overall situation is presented in *Table 2.* The high molecular weight 100 grade showed a very restricted range of temperature for successful drawing. The results for the 500 and 8010 grades were more remarkable in that the slow cooled samples showed failure normally occurring before the sample had even begun to neck. Quenched samples, on the other hand, showed good drawing over a wide temperature range and a maximum draw ratio of 23 was obtained for Delrin 500 drawn at 144°C, with a 10 sec 0.1% Young's modulus of 39.5 GPa. This modulus value is a little higher than the maximum values for ultra-oriented POM reported by Clark and Scott[4].

The maximum draw ratio was highly dependent on temperature, and in the temperature range 98°–125° Delrin 500 and 8010 would only draw to comparatively low draw ratios (i.e. < 10).

The influence of draw temperature is summarized by *Figures 1* and *2.* In *Figure 1* the maximum draw ratio obtainable at each temperature is shown for quenched samples of each of the three grades. There is a clear molecular weight effect in that the 100 grade with the highest molecular weight shows a lower peak draw ratio than either the 500 or 8010 grades. The 500 grade achieves somewhat higher draw ratios than the 8010 grade. These results are quite similar to those observed previously for LPE and PP. As in those polymers the highest draw is obtained with low molecular weight polymer. As the molecular weight is reduced to very low levels, however, the possibility of brittle fracture can limit the draw ratio.

There is also the question of the effectiveness of the drawing process with regard to the production of oriented high modulus material. *Figure 2* shows clearly that for an intermediate draw ratio (λ = 13) (after a broad peak modulus plateau centred on 145°C) above 150°C the modulus decreases with increasing draw temperature. The effect of draw temperature on the modulus/draw ratio relationship is brought out in more detail for the 500 grade by the results shown in *Figure 3* for drawing this material at 145° and 164°C, respectively. It can be seen that at 145°C, not only is higher draw ratio possible, but also that the drawing is more effective. This result is similar to that obtained in PP and for high molecular weight samples of LPE. The yield stress (measured for the 500 grade) falls quite rapidly in a linear fashion over the whole temperature range (*Figure 4*) which is well below the melting point of the polymer. These results are consistent with the conclusions expressed in previous papers on LPE[7], that the drawing of crystalline polymers is controlled by the deformation of a molecular network which embraces both crystalline and non-crystalline material. The higher yield stresses at the lower temperatures reflect the higher stresses transmitted through the structure as a whole, which are required to produce effective draw i.e.

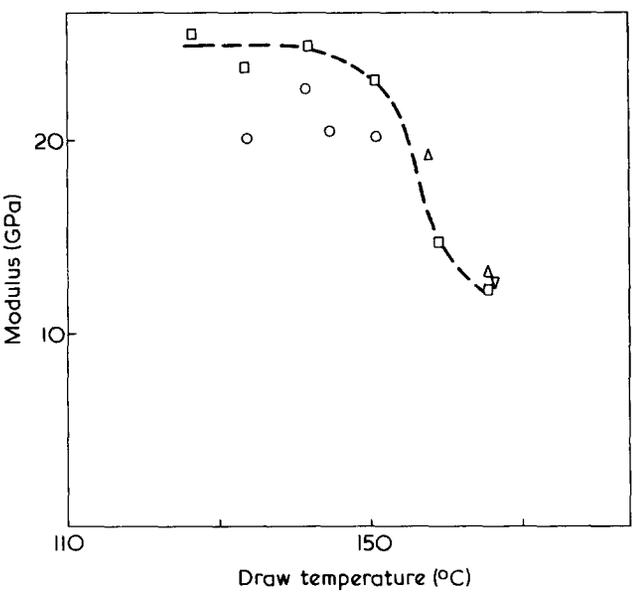

Figure 2 Modulus vs. draw temperature at a constant draw ratio of 13. □, Delrin 500 (200/W); ○, Delrin 8010 (200/W); △, Delrin 100 (200/W); ▽, Delrin 100 (200/SC)

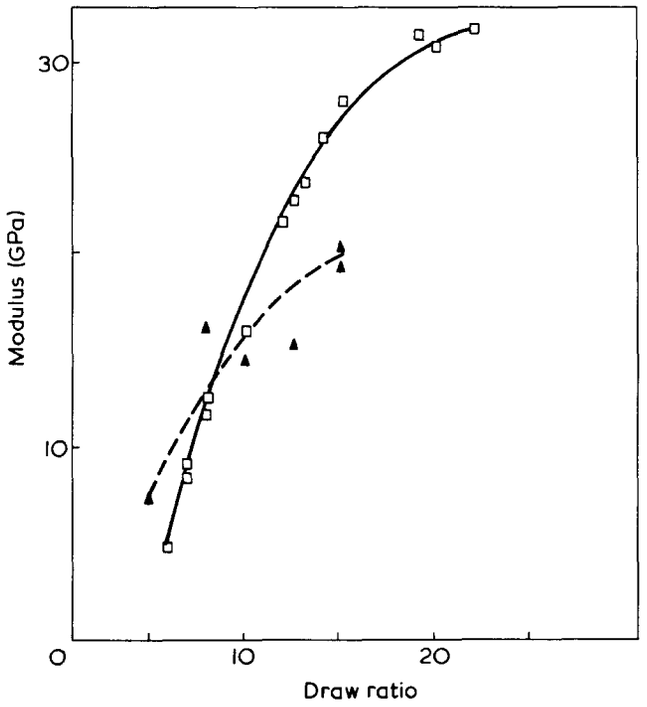

Figure 3 Modulus vs. draw ratio at different temperatures. □, Delrin 500 (200/W), 10 cm/min at 145°C; ▲, Delrin 500 (200/W) 10 cm/min at 164°C

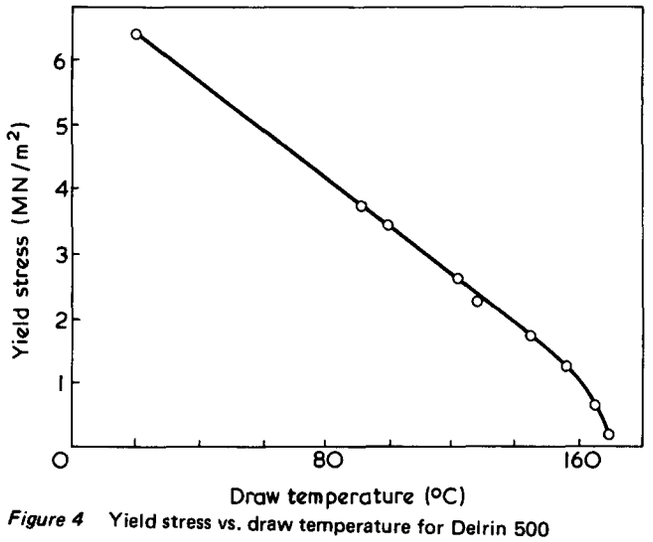

Figure 4 Yield stress vs. draw temperature for Delrin 500

molecular alignment leading to high modulus, as distinct from flow drawing. This phenomenon is common to both crystalline and amorphous polymers and has been well documented for the drawing of amorphous poly(ethylene terephthalate)[8]. There is a definite molecular weight effect in this respect, as shown by *Figure 5* where it can be seen that the higher molecular weight D500 grade shows a higher modulus for a given draw ratio than the D8010 grade for identical drawing conditions. Considerable attempts were made to draw the highest molecular weight grade (D100) to high draw and high modulus by increasing the drawing temperature. These were not successful as shown by the results in *Figure 6*, which is similar to the situation in LPE, and confirms that the molecular weight effects reported for that polymer and also for PP also apply to POM.

The results discussed so far are similar to these reported previously for the drawing behaviour of LPE and PP in showing effects of initial thermal treatment, molecular weight and draw temperature. The results described so far suggest that within the range examined the optimum molecular weight for high draw and high modulus is the D500 grade with $\bar{M}_w \sim 90\,000$. In terms of the degree of polymerization this is lower than the optimum molecular weight range for polyethylene and polypropylene. The difference could lie in the different molecular structure, the presence of oxygen atoms in the chain perhaps increasing the intermolecular forces.

Further detailed studies were concentrated on the D500

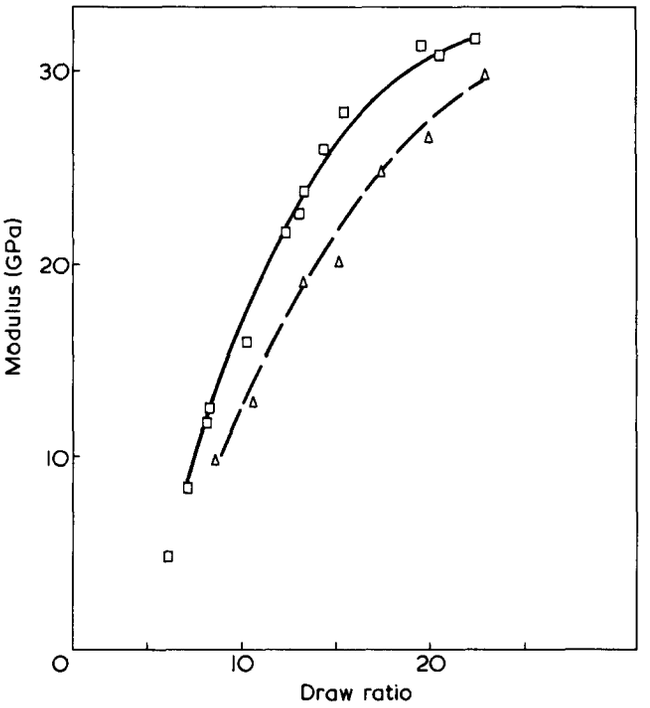

Figure 5 Modulus vs. draw ratio for Delrin 500 and Delrin 8010. □, Delrin 500 (200/W) 10 cm/min at 145°C; △, Delrin 8010 (200/W) 10 cm/min at 144°C

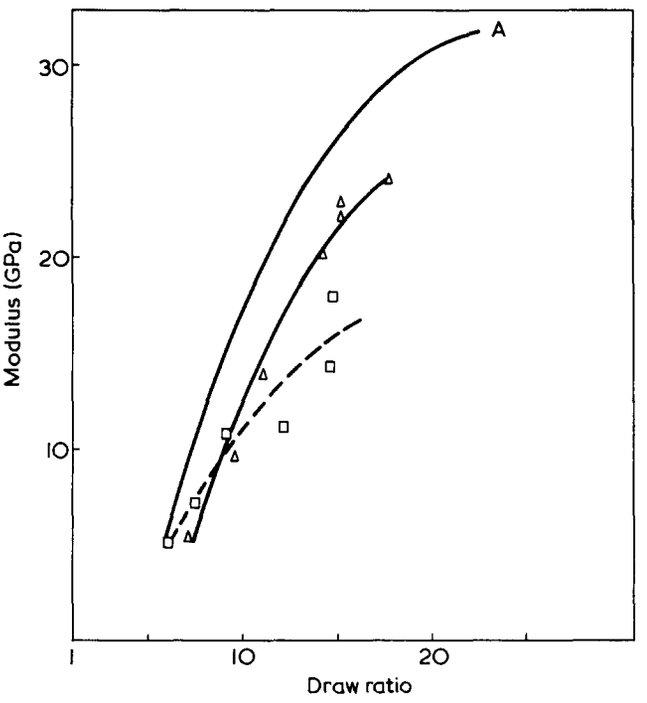

Figure 6 Modulus vs. draw ratio for Delrin 500 and Delrin 100. A, Delrin 500 (200/W) 10 cm/min at 145°C; △, Delrin 100(200/W) 10 cm/min at 162°C; □, Delrin 100 (200/SC), 10 cm/min at 160°C

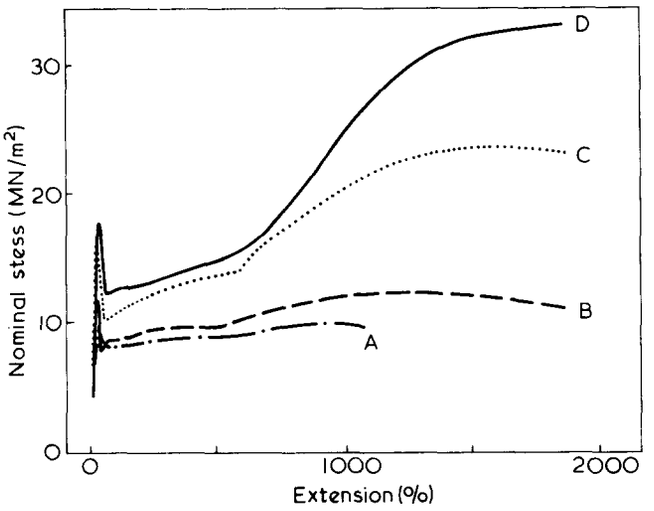

Figure 7 Nominal stress vs. extension for Delrin 500 (draw temperature 145°C). A, 0.2 cm/min; B, 1 cm/min; C, 10 cm/min; D, 50 cm/min

grade, and a careful examination was undertaken of the influence of strain rate. The key results are summarized in *Figures 7* and *8*. From these Figures it can be seen that the strain hardening behaviour during hot drawing is markedly dependent on strain rate (*Figure 7*), and that there is an optimum strain rate in the region of 1 cm/min crosshead speed for achieving high modulus with high draw (*Figure 8*). *Figure 7* shows that after the initial yield at low strains, drawing proceeds at approximately constant load up to an overall draw ratio of 6–7. At the lowest strain rate of 0.2 cm/min the sample fails at a comparatively low draw ratio. At the higher strain rates, on the other hand, subsequent draw involves a further increase in load, which is quite dramatic at the highest strain rate. It is remarkable that the modulus for a given draw ratio is, however, significantly greater at the lower crosshead speed of 2 cm/min.

The results are consistent with the general ideas of Peterlin[9] in that the initial stage of the drawing process involves the transformation from a spherulitic to a fibrillar structure which is completed by draw ratio 6–7. The second stage of the drawing process consists of redrawing the fibrillar structure. It appears from our investigation that for this redrawing to produce the highest modulus value in the drawn material, not only must there be a temperature in a comparatively narrow range ~145°C but that the strain rate must also be closely prescribed. These complex requirements for optimization are consistent with our view that the drawing of crystalline polymers[7] involves both the crystalline and non-crystalline regions in the deformation process, and suggest that there must be a suitable coincidence of rate processes involving both phases. If a single process were involved, there would clearly be an equivalence between temperature and strain rate. For example if only the amorphous material were involved we might expect that increasing strain rate and temperature together in a suitable manner would still give effective draw (as in amorphous PET). But if it is also necessary to involve a specific crystal deformation process then it will be necessary for the rate at which this process is occurring to coincide with that for the deformation of the amorphous material, and this coincidence will only occur at a specific temperature.

Two-stage drawing

Clark and Scott[4] produced ultra-high modulus POM by a two-stage drawing process. Considerable emphasis was placed on the fact that the drawing was carried out in two stages. In the first stage the spun fibres were drawn to the natural draw ratio[1] of about 7 at a fast draw rate on conventional textile equipment. It was stated that to obtain ultra-high modulus a second stage of draw was then required which had to be carried out under quite different conditions from the first draw. In the previous work on LPE and PP the idea of a natural draw ratio has been refuted, and it is clear that the material through the neck is also being drawn. It therefore appeared of some interest to examine two-stage drawing further in the light of the results presented here. An additional reason for this is that the materials produced here by single stage drawing appeared to be marginally superior in modulus to those produced by Clark and Scott in two stage drawing (~40 GPa as against 35 GPa at draw ratio 20).

We have therefore performed two-stage drawing as follows. In the first stage the 2 cm gauge length samples were extended at a crosshead speed of 10 cm/min for 72 sec ($\lambda \simeq 7$, the 'natural' draw ratio) then redrawn either at the same speed, or at the slower speed of 1 cm/min. *Figures 9* and *10* compare two-stage drawing with one-stage drawing at the same temperature (145°C). In contrast to what might seem to have been implied by the work of Clark and Scott, there is apparently no advantage to be gained from two-stage drawing *per se*. On the contrary, single-stage drawing at 10 cm/min produces higher modulus material than two-stage drawing (*Figure 9*). This was explored further by reducing the strain rate in the second-stage draw, but the results (shown in *Figure 10*) show a similar advantage for the single-stage draw process. We believe that this can be attributed to the annealing effects which occur when the sample is returned to the high temperature enclosure prior to the second stage of drawing.

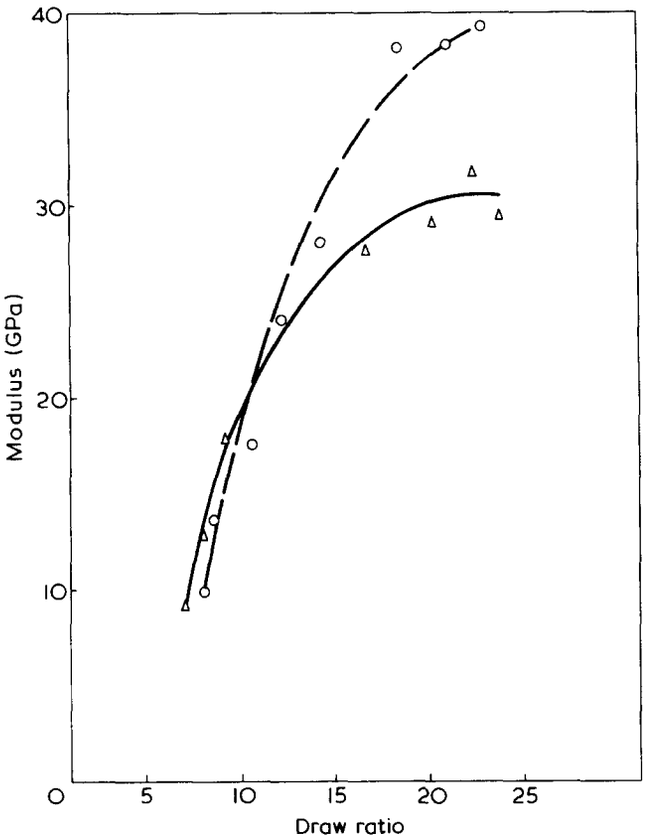

Figure 8 Modulus vs. draw ratio at different draw rates. ○, Delrin 500 (200/W) 1 cm/min at 145°C; △, Delrin 500 (200/W) 10 cm/min at 145°C

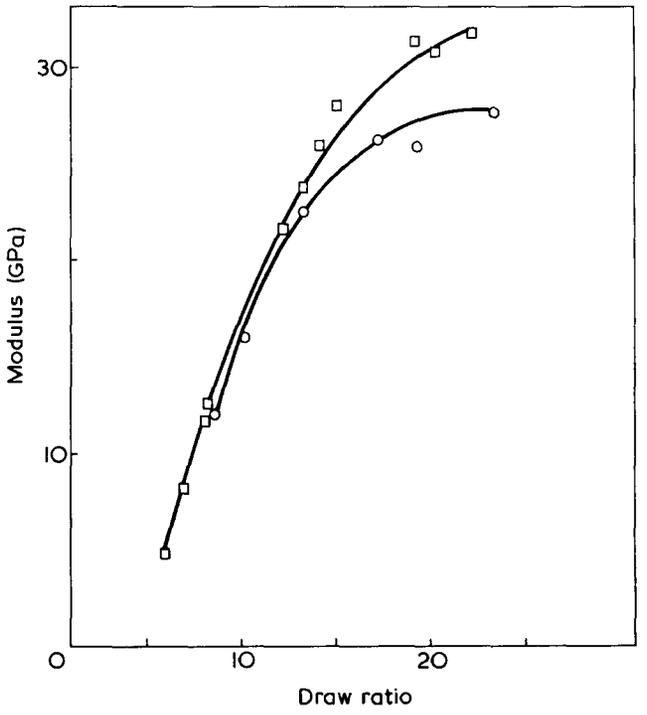

Figure 9 Modulus vs. draw ratio for single and two stage drawing. □, Delrin 500 (200/W) 10 cm/min at 145°C; ○, Delrin 500 (200/W) 10 cm/min for 72 sec at 145°C. Redrawn 10 cm/min at 145°C

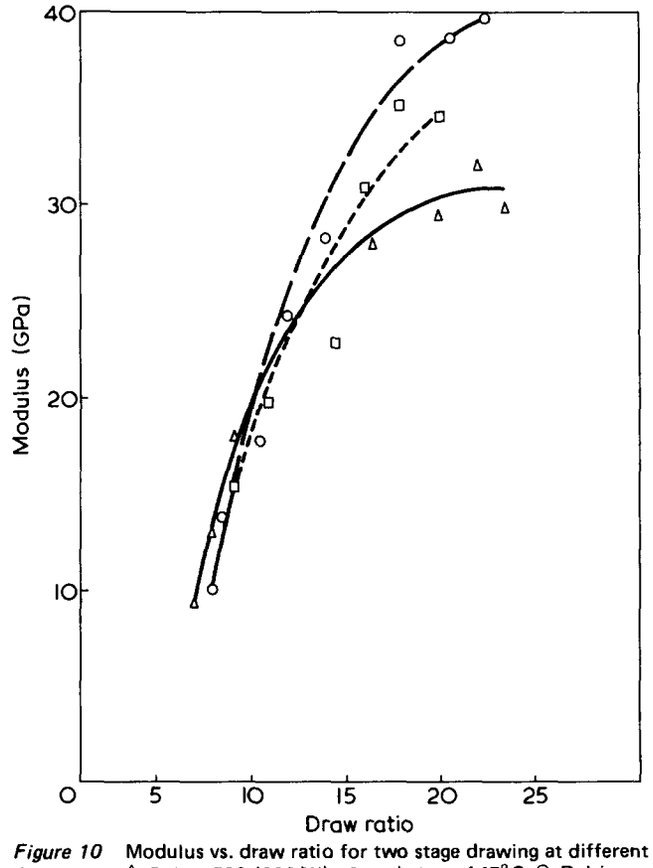

Figure 10 Modulus vs. draw ratio for two stage drawing at different draw rates. △, Delrin 500 (200/W) 10 cm/min at 145°C; ○, Delrin 500 (200/W) 1 cm/min at 145°C; □, Delrin 500 (200/W) 10 cm/min for 72 sec at 145°C. Redrawn 1 cm/min at 145°C

Because of the possibility that even higher modulus material might be produced, further studies of two-stage drawing were undertaken in which the second stage of drawing was performed at a slightly higher draw temperature of 150°C. These results are shown in *Figure 11*. It can be seen that samples drawn initially at a crosshead speed of 10 cm/min for 72 sec at 145°C and then redrawn at 1 cm/min at 150°C lie on a slightly lower modulus/draw ratio curve than those in which both drawing stages were at 145°C. Samples drawn at 10 cm/min at 145°C and then redrawn at 150°C lie on the same modulus draw ratio curve as those redrawn at 1 cm/min at 150°C.

These results suggest that there is no advantage to be gained from two-stage drawing. The slightly higher moduli which have been achieved in this investigation by single-stage drawing may be due to the adverse effects of annealing which may occur prior to the second stage in the two-stage process. These effects are quite small, as can be seen from the stress–strain curves for the two-stage draw process shown in *Figure 12*. For two-stage drawing the first stage was stopped at λ

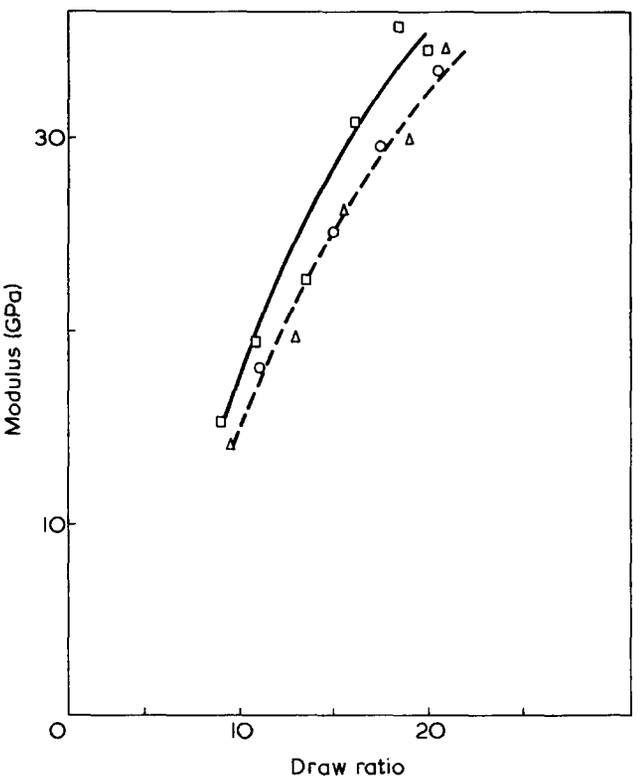

Figure 11 Modulus vs. draw ratio for two stage drawing at different draw temperatures. □, Redrawn 1 cm/min at 145°C; △, redrawn 1 cm/min at 150°C; ○, redrawn 10 cm/min at 150°C

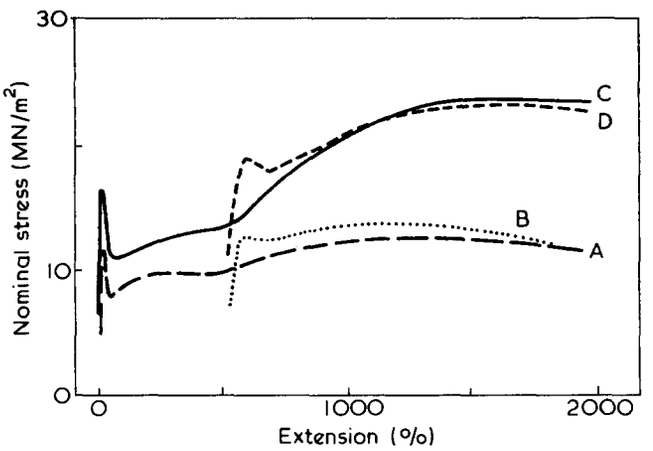

Figure 12 Nominal stress vs. extension for single and two stage drawing. A, B 1 cm/min (B redrawn); C, D 10 cm/min (D redrawn)

Table 3 Summary of X-ray measurements

Material	Drawing conditions	Draw ratio	Young's modulus (GPa)	2θ	$(\Delta\theta)_{1/2}$ Meridional scan	$(\Delta\theta)_{1/2}$ Equatorial scan
Delrin 500 (200/W)	10 cm/min 144°C	23	27.0	22.9	0.85	3.8
	10 cm/min 143°C	13	23.7	22.8	0.85	3.9
	1 cm/min 145°/C	22.5	30.7	22.9	0.75	2.8
	10 cm/min for 72 sec at 145°C. Redrawn 10 cm/min at 145°C	22.5	27.3	22.8	0.8	5.3

~ 7, the sample removed from the high temperature oven and redrawn later. It appears that the second part of the stress–strain curve for the interrupted drawing is identical to that for single stage drawing, except for a small apparent second yield process. This may be due to a small part of the sample which has not drawn fully to its natural draw ratio in the first stage.

It is particularly notable that the effects of strain rate on the strain hardening are exactly reproduced for two-stage drawing. For example, if the sample is drawn at 10 cm/min for 72 sec and then redrawn at 1 cm/min, the first part of the stress–strain curve corresponds to the single-stage 10 cm/min stress–strain curve and the second part to the 1 cm/min single stage stress–strain curve.

Apart from the loss in modulus caused by annealing we can see therefore that the strain rate effects are identical in single-stage and two-stage drawing. Thus two-stage drawing at a crosshead speed of 10 cm/min for both stages produces lower modulus material than single-stage drawing at this crosshead speed. Two stage materials drawn at 10 cm/min, followed by 1 cm/min have a higher modulus than single stage materials drawn at 10 cm/min but lower than single-stage materials drawn at 1 cm/min.

X-ray measurements

Both equatorial and meridional scans of the (009) reflection were made. The angular width in the equatorial scan where the intensity is half $(\Delta\theta)_{1/2}$ provides a semiquantitative measure of the crystallite orientation, as this quantity decreases with increasing orientation[10]. Similarly, the angular width $(\Delta\theta)_{1/2}$ for the meridional scans, recalling the Scherrer equation[11], provides a quantity which is inversely proportional to the longitudinal crystal thickness.

The results are summarized in *Table 3*. First, the meridional scans show that there are no appreciable changes in the apparent longitudinal crystal thickness for major changes in the drawing procedure. The equatorial scans, on the other hand, do reveal systematic differences which correlate with the modulus results. In particular samples drawn at 1 cm/min show appreciably greater crystallite orientation than those drawn at 10 cm/min which is consistent with their higher modulus. There is also a considerable difference between single-stage and two-stage drawn material, the latter showing a lower degree of crystallite orientation. It is considered that this could be due to the annealing which occurs in two-stage drawing prior to the second stage and permits some degree of disorientation of the crystalline regions.

D.s.c. measurements

As shown in *Figure 13*, the melting point of material drawn in a single stage at 145°C increased from 179° at $\lambda = 8$ to

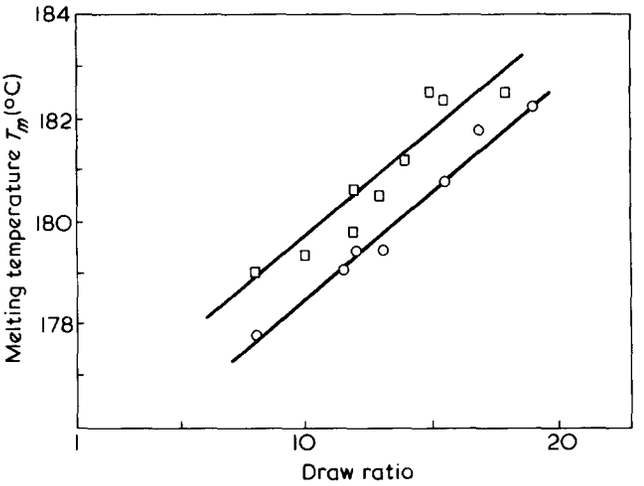

Figure 13 Melting temperature T_m vs. draw ratio at different draw rates. □, 10 cm/min at 144°–145°C; ○, 10 cm/min at 165°–166°C

183°C at $\lambda = 18$. A similar systematic increase in melting point from 177.5°C at $\lambda = 8$ to 181.8°C at $\lambda = 18$ was observed for single-stage material drawn at 165°C. There were significant differences between single-stage and two-stage drawing. For example, two-stage drawing where the first and second stages were at 145° and 165°C, respectively, showed a much more rapid increase in melting point with draw ratio viz 179.3°C at $\lambda = 11$ to 183.5°C at $\lambda = 17$. These increases in melting point with increasing draw ratio are comparable in magnitude to those observed for LPE[1] where differences between different preparation methods were also observed. In some instances, for samples with $\lambda > 15$, a second melting peak was observed at a higher temperature (typically 2°–3°C above the main peak).

CONCLUSIONS

It has been shown that the drawing behaviour of POM is very similar in many respects to that of LPE and PP. In particular there is an optimum temperature range for drawing polymers of given molecular weight, as observed for LPE and PP. Unlike LPE and PP, however, it appears that there is a very narrow range of strain rate which has to be coupled with the optimum temperature to achieve high modulus material. It is suggested that this is due to very tight constraints on the optimization of the plastic deformation process which involves both crystalline and non-crystalline material in the polymer. This may impose severe limitations on the development of a commercially viable process for high modulus POM. It also appears that the drawing behaviour is molecular

weight dependent, as in LPE and PP. Within the range examined the optimum grade for high draw and high modulus is the D500 grade.

There would not appear to be any advantages to be gained from two-stage drawing, as might have appeared to be implied by previous work. On the contrary, there are indications that the optimum single-stage drawing process gives slightly higher modulus products than the optimum two stage drawing process.

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