Effect of draw rate on the stress–strain behaviour of polymers

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A new phenomenon has been observed in the tensile deformation of polymers, including polypropylene, poly(ethylene terephthalate) and polyethylene. It has been seen that when draw rate is larger than a critical value, Young's modulus, yield stress and other parameters associated with the drawing response of these polymers decrease rapidly with the increasing draw rate; the normal time–temperature superposition principle does not appear to hold in this case. Further it can be shown that this decrease in modulus and yield stress is not caused by a temperature rise during drawing; the tensile deformation process before yield is largely isothermal. As an alternative, a change in the yield mechanism is suggested as a reason for the decrease in modulus and yield stress. This decrease may arise from void formation and crazing, which is relatively uniform throughout the sample, and dominates at these high draw rates.

(Keywords: draw rate; stress–strain; modulus; tensile deformation)

INTRODUCTION

The effect of speed testing on the stress–strain behaviour of polymers has been investigated for some time[1–7]. It is generally considered that the behaviour observed is approximately what one would expect on the basis of the time-temperature superposition principle, namely, modulus and yield strength both increase as the rate of testing increases. However, the time–temperature principle holds only in a limited temperature range. If the test temperature is lower than the glass temperature (T_g), a polymer is brittle and hard; however, it can undergo a dramatic change in response as temperature is raised through T_g. Similarly, it will be shown that modulus and yield strength increase only over a limited range of increased testing rates, before a similar change in response is observed. In this present work we have studied the effect of a wide range of draw rates on both modulus and yield strength of some polymers. Decreases in modulus and yield strength have been observed for polypropylene, polyethylene and poly(ethylene terephthalate) drawn at high rates; a possible reason for these phenomena is discussed.

EXPERIMENTAL

Materials

The polypropylene used was a commercial sheet described as Polypropylene 5225 and manufactured by Shell Development Co. This was a translucent sheet of thickness 0.8 mm containing no plasticizer but including small amounts of stabilizers. Its number-average molecular weight M_n is 50 000 and weight-average molecular weight M_w is approximately 600 000. Both the poly(ethylene terephthalate) and the high-density polyethylene used were sheet materials obtained from Dupont and Shell Development Co., respectively. The sheet thickness of poly(ethylene terephthalate) was 1.04 mm and that of high-density polyethylene was 0.79 mm; no futher characterization was made available.

Test methods

Stress–strain curves of materials during cold drawing were cut into strips of the usual dumb-bell shape with a die were cut into strips of the usual dumbbell shape with a die (ASTM D638-V). Test specimens were extended at various rates from 0.5 to 100 cm min^{-1}. Yield and drawing stress were calculated as the ratios of the yield load and drawing load to the original cross-sectional areas. Since the stresses are based on original cross-sectional area, they are 'conventional' rather than 'true' stresses. Extensional moduli of the specimens were also obtained from Instron measurements by calculating the initial slopes of the load-elongation curves. The natural draw ratio was obtained from the ratio of the length of a cold-drawn region to the length of the same material before it was stretched. Every measurement was repeated 30 times at least. The error of the experimental results is less than $\pm 10\%$. The experimental error at low draw rates is less than that at high draw rates.

A thermostated water bath, in which the water level can be controlled, was fixed on and surrounded the lower grip. Specimens can be drawn either completely or partially under water. The temperature of the bath could be controlled over the range from 22 to 90°C with an accuracy of 0.1°C. The appearances of drawn and undrawn specimens were observed using an optical microscope (Olympus model BHA). Approximate densities of undrawn and drawn specimens of polypropylene were measured by titration using a stirred isopropanol–water system.

RESULTS AND DISCUSSION

The stress–strain behaviour of polymeric materials is dependent on draw rate[8]. Cold drawing of polypropylene at 2.5, 5 and 12.5 cm min^{-1} has been reported by Lee and Uhlmann[9]; in this present work the range of draw rates (R_d) was expanded from 0.5 to 100 cm min^{-1}. *Figure 1* shows typical tensile load–elongation curves of

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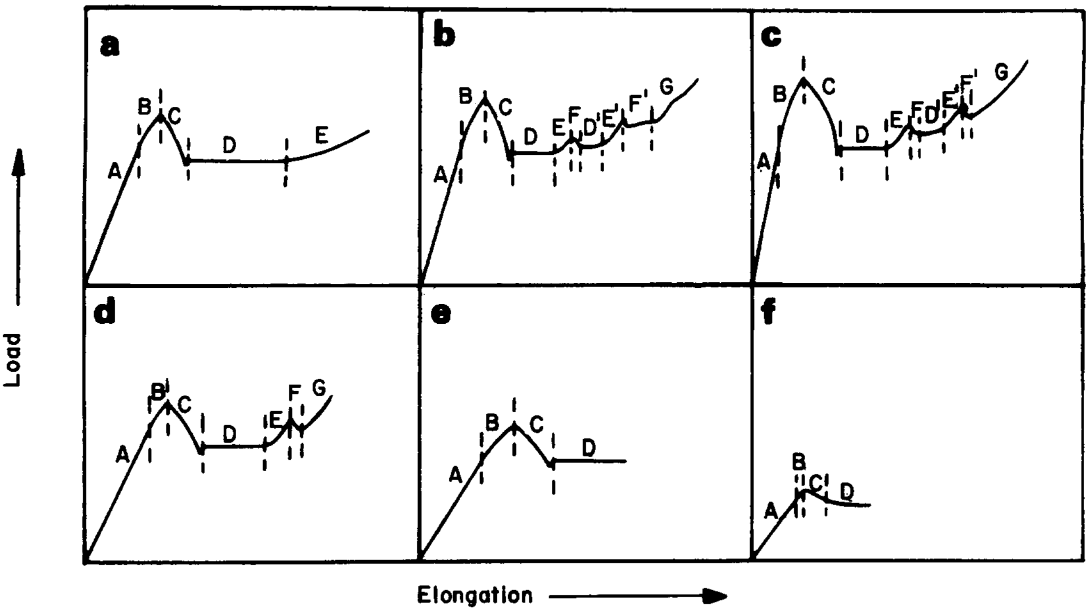

Figure 1 The effect of draw rate on the load–elongation curve of polypropylene: (a) $R_d = 0.5\,\mathrm{cm\,min^{-1}}$; (b) $R_d = 2.5\,\mathrm{cm\,min^{-1}}$; (c) $R_d = 10\,\mathrm{cm\,min^{-1}}$; (d) $R_d = 25\,\mathrm{cm\,min^{-1}}$; (e) $R_d = 50\,\mathrm{cm\,min^{-1}}$; (f) $R_d = 100\,\mathrm{cm\,min^{-1}}$

polypropylene at different draw rates at room temperature. It is clear that the response of polypropylene to such tests is largely influenced by draw rate. The main macroscopic features include:

(1) shape of the load–elongation curve,
(2) ratio of yield stress to drawing stress,
(3) modulus and yield stress,
(4) drawing stress,
(5) natural draw ratio,
(6) yield strain,
(7) stress to break, and
(8) work to break.

On initial elongation of a specimen (region A), the curve is linear and deformation is relatively homogeneous. In region B, the curve becomes nonlinear, and a neck begins to form and becomes visible in region C. This neck initially forms with an asymmetric cross section if viewed in a plane perpendicular to the specimen and parallel to the draw direction. On further drawing the neck becomes symmetric and propagates over some length. By the end of region C one boundary of the neck is moving more rapidly into the undeformed material than the other boundary. In region D the neck is propagating in a constant and reproducible manner. When the draw rate is equal to or less than $1\,\mathrm{cm\,min^{-1}}$, the neck first propagates in the direction corresponding to the original moving neck boundary. However, as the shoulder of the gauge is approached, propagation of the neck decreases in the original direction, eventually stops, and then increases in the opposite direction. The two gauge shoulders are approached at almost the same time in the two directions; on further extension the load increases and the sample eventually breaks (*Figure 1a*).

At moderate draw rates (2.5, 5 and $10\,\mathrm{cm\,min^{-1}}$) two small peaks appear in the load–elongation curve after region D (*Figures 1b* and *1c*). At first, the gauge shoulder near the rapidly moving end of the neck region is approached, and the neck propagates in only one direction (region D). In region E, the neck propagates into the shoulder of the gauge and the load required for drawing the sample increases. In region F yielding has transferred to the other end of the neck with the neck boundary becoming more abrupt. Propagation then continues in this direction (region D′) until the other shoulder is reached (region E′). In the final portion of the curve, either the first shoulder will yield and the direction reverse again, or further drawing of the neck will occur (refion F′ and region G).

When the draw rate is equal to $25\,\mathrm{cm\,min^{-1}}$, propagation of the neck can reach the first shoulder, but the sample typically breaks after reversal of the neck direction, before the other shoulder is approached, i.e. there is only one small peak after region D (*Figure 1d*). At high draw rates (50 and $100\,\mathrm{cm\,min^{-1}}$), the sample is easily broken, and the neck does not reach either of the two shoulders in the sample (*Figures 1e* and *1f*).

The ratio of yield stress to drawing stress (σ_y/σ_d) is a useful index for characterizing the draw behaviour of polymers[10]. It can be easily obtained from the load–elongation curve by dividing the height of the peak (region B and C) by the height of the trough (region D). If the ratio is unity, the specimen has extended uniformly. If the ratio is much greater than unity, the specimen has cold drawn. *Figure 2* shows the effect of draw rate on the ratio (σ_y/σ_d) for polypropylene. When draw rate is equal to or less than $10\,\mathrm{cm\,min^{-1}}$, the ratio increases with increasing draw rate and polypropylene shows an increased ability to cold draw. At $R_d > 10\,\mathrm{cm\,min^{-1}}$, the ratio decreases rapidly with increasing draw rate; for example, at $R_d = 100\,\mathrm{cm\,min^{-1}}$ the ratio is ≈ 1.0, and polypropylene is extending almost uniformly.

It is observed that changes in modulus and yield stress of polypropylene are also non-uniform with increasing draw rate. As the draw rate is increased, but less than $10\,\mathrm{cm\,min^{-1}}$, modulus and yield stress increase. However, one observed a decrease in both modulus and yield stress once draw rate exceeds $10\,\mathrm{cm\,min^{-1}}$. *Figures 3* and *4* clearly show the reported changes of Young's modulus and yield stress of polypropylene as a function of draw rate in air. The importance of the response in water will be discussed a little later in the paper.

It is believed that this is the first report of the

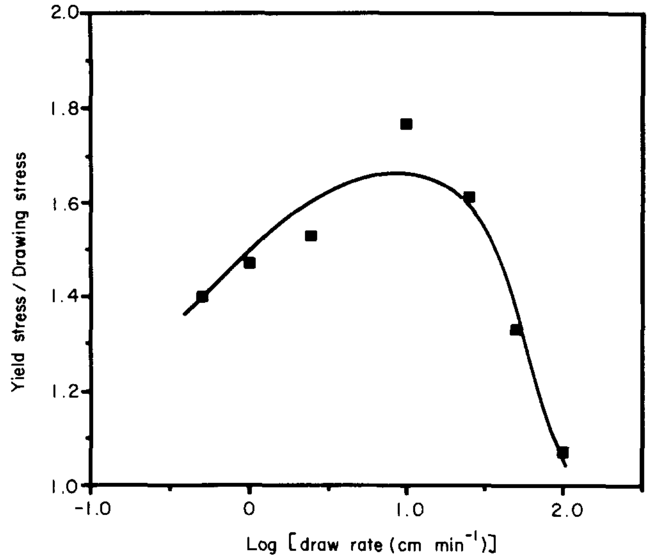

Figure 2 The effect of draw rate on the ratio of yield stress to drawing stress of polypropylene

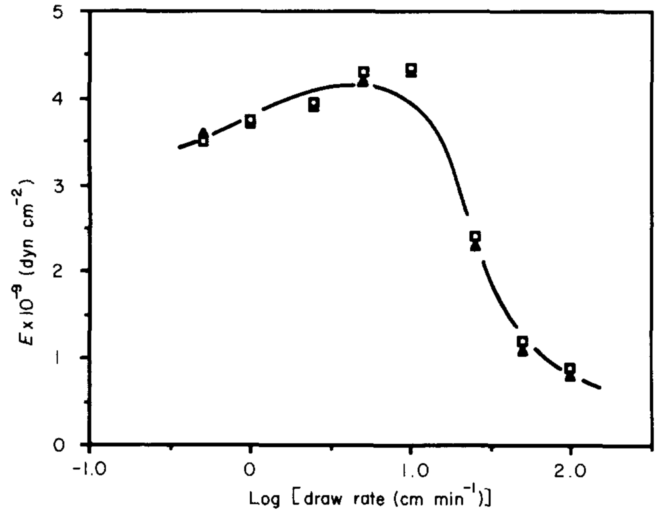

Figure 3 The effect of draw rate on the modulus of polypropylene drawn in air (▲) and under water (☐)

phenomena of modulus and yield stress decreasing with increasing draw rate at high draw rates. However, the observation that the drawing stress decreases with increasing draw rate has been observed by Ward and coworkers[11] for poly(ethylene terephthalate). Experimental results for the drawing stress of polypropylene in air show the same trend. *Figure 5* shows the influence of draw rate on drawing stress of polypropylene. Initially there is a slight increase of drawing stress with draw rate; subsequently, the slope of the drawing stress–log(R_d) curve decreases until the drawing stress passes through a minimum value. This minimum in drawing stress for polypropylene is located at $R_d = 10$ cm min^{-1}, which is approximately the same rate as the maximum observed in the modulus and yield stress plots. The authors are aware that these data could also reasonably fit a more or less horizontal straight line; however, see ref. 11 for a similar report on poly(ethylene terephthalate).

It is generally agreed that the decrease in drawing stress is caused by a temperature rise in the neck area. When drawing is carried out at a low rate, any heat generated will be conducted away from the neck sufficiently rapidly that no temperature rise occurs. However, as the rate of drawing is increased, the process becomes more nearly adiabatic. This will lower the drawing stress, and thus reduce the force necessary to propagate the neck. Calculated data by Ward[11] for poly(ethylene terephthalate), together with experimentally measured temperature rises reported by Vincent[10] for polyethylene and poly(vinyl chloride), show that adiabatic heating effects become important as the draw rate is raised above approximately 1 cm min^{-1}. It is presumably no coincidence that this is where we observe an initial decrease in the drawing stress of polypropylene. The decrease of drawing stress with increasing draw rate is actually due to changes in temperature and is not an effect of draw rate itself.

Liu and Harrison[12] modelled the movement of a neck during drawing as a small flat plate immersed in a stream of fluid, in steady flow, and oriented parallel to the plate. Heat loss during necking is mainly caused by forced-convection heat transfer. Resistance to heat transfer is

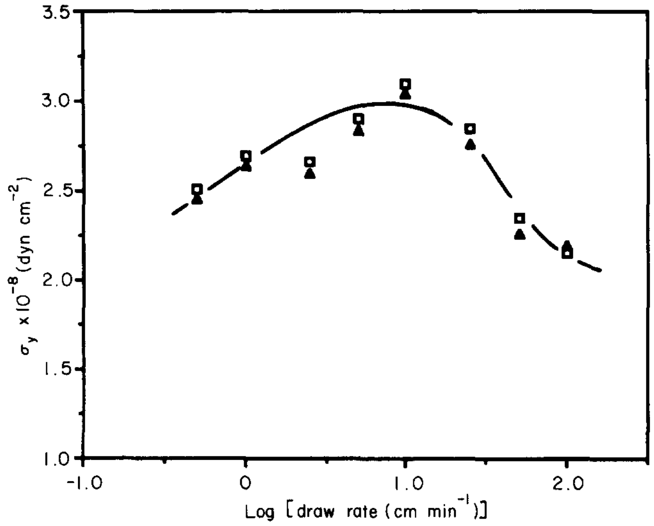

Figure 4 The effect of draw rate on the yield stress of polypropylene drawn in air (▲) and under water (☐)

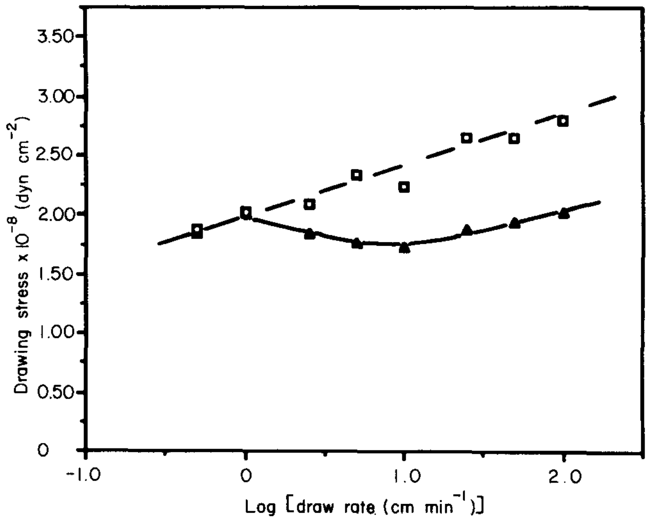

Figure 5 The effect of draw rate on the drawing stress of polypropylene drawn in air (▲) or under water (☐)

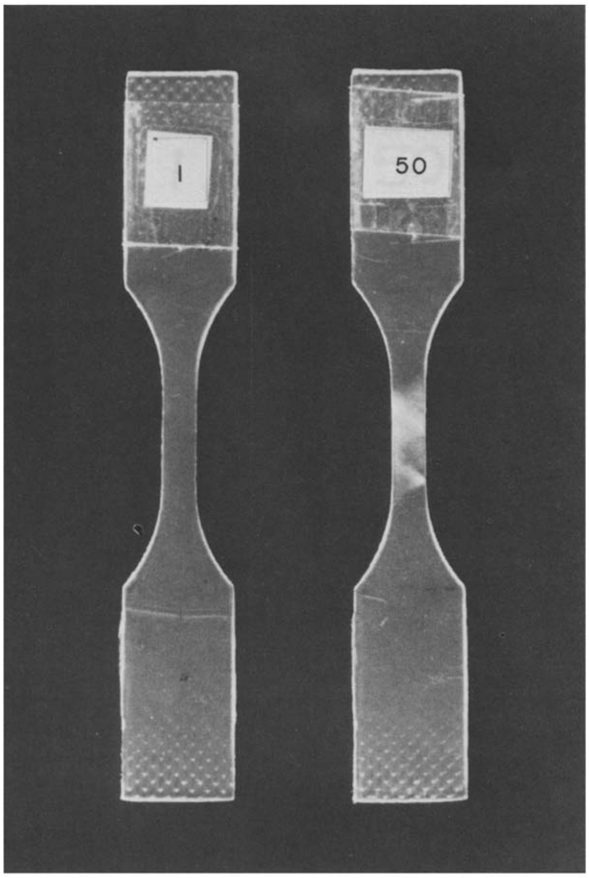

Figure 6 The appearance of polypropylene drawn just prior to yield point at (a) $R_d = 1$ cm min^{-1} and (b) $R_d = 50$ cm min^{-1}

concentrated primarily in a thin layer immediately adjacent to the surface of the boundary layer, and heat transfer is determined by the relative contributions of convective and conductive transport within this boundary layer. Based on calculations with this model, the ratio of the heat transfer coefficient for a sample drawn under water to that for a sample drawn in air is ≈ 70. So, extension of a sample under water prevents substantial local heating due to the high thermal conductivity of water compared to air. The results of drawing stress measurements on polypropylene drawn under water are represented by the broken line in *Figure 5*. The obvious contrast between the shapes of the full curve and broken line is due to the effects of temperature on the drawing sample.

In contrast, the decreases in modulus and yield stress of polypropylene at high draw rates are not caused by a temperature rise in the neck area. Modulus and yield stress measurements on polypropylene drawn under water are shown in *Figures 3* and *4*. The results show that within the range of error of the experiments both modulus and yield stress for polypropylene drawn under water are essentially the same as those for polypropylene drawn in air; this similarity is maintained even at $R_d = 100$ cm min^{-1}.

These observations demonstrate that before yielding the extension force only serves to reorganize the sample and does not produce heat; the pre-yielding processes in polypropylene are essentially isothermal. Springer and coworkers[13] have investigated force–elongation curves and temperature profiles of polypropylene. Neck temperature was measured with an i.r.-radiation thermometer, and their results showed that until the sample yields the temperature is effectively constant. This observation also directly supports the concept that the pre-yielding process of polypropylene is approximately isothermal.

The appearance of samples drawn at $R_d = 1$ and 50 cm min^{-1} just prior to the yield point are shown in *Figure 6*. At $R_d = 1$ cm min^{-1} the sample remains translucent throughout the gauge. At $R_d = 50$ cm min^{-1} the sample is white–opaque in one or more regions of the gauge and shear deformation bands appear. The extent of opacity increases as draw rate increases.

This opacity is caused by the formation of microvoids. *Figure 7* shows optical microscope pictures of polypropylene drawn at 1 and 50 cm min^{-1} just prior to yield. As previously noted the sample drawn at $R_d = 1$ cm min^{-1} remains translucent throughout the gauge length and almost no microvoid formation is observed (*Figure 7a*). When $R_d = 50$ cm min^{-1}, the sampling area is selected at a white–opaque region and it is clear that there are a lot of microvoids present (*Figure 7b*). Experimental results show that both the quantity and size of microvoids formed prior to any nominal 'yield' point increase rapidly as draw rate increases.

The above results are also consistent with observed density changes. The density of the original polypropylene (ρ_0) is 0.881 g cm^{-3}; ρ_y is the density just prior to the yield point for polypropylene and ρ_d is the density of the sample drawn to its natural draw ratio. Let $\Delta\rho_1 = \rho_0 - \rho_y$ and $\Delta\rho_2 = \rho_y - \rho_d$; changes in $\Delta\rho_1$ and $\Delta\rho_2$ with draw rate are shown in *Figure 8*. When $R_d > 10$ cm min^{-1} the decrease in bulk sample density during drawing takes place primarily before yield. When $R_d < 10$ cm min^{-1}, sample density decreases take place primarily after yield. Microvoids are apparently formed before yield at $R_d > 10$ cm min^{-1} while the formation of microvoids happens after yield at $R_d < 10$ cm min^{-1}.

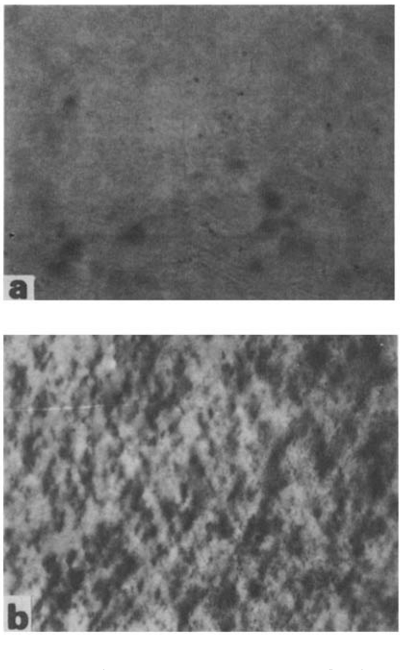

Figure 7 The effect of draw rate on microvoids of polypropylene drawn at (a) $R_d = 1$ cm min^{-1} and (b) $R_d = 50$ cm min^{-1}

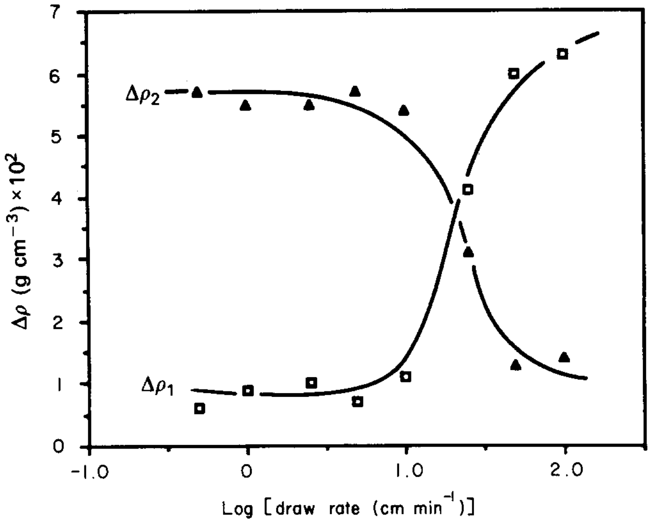

Figure 8 The effect of draw rate on $\Delta\rho_1 = \rho_0 - \rho_y$ and $\Delta\rho_2 = \rho_y - \rho_d$ of polypropylene

Table 1 Volume per cent microvoids formed *versus* draw rate

R_d (cm min^{-1})	$\frac{\rho_d^{-1}-\rho^{-1}}{\rho^{-1}} \times 100$ (%)
0.5	7.97
1.0	8.23
2.5	8.36
5.0	8.36
10.0	8.63
25.0	9.65
50.0	9.58
100.0	9.99

The ρ_d of all samples drawn at different rates is less than the density of amorphous polypropylene (ρ_a). The crystallinity of samples drawn to their natural draw ratio at different draw rates has been previously measured by d.s.c.[14] Using these d.s.c. values of crystallinity and accepted values for crystalline and amorphous density of polypropylene ($\rho_c = 0.935$ g cm^{-3}, $\rho_a = 0.854$ g cm^{-3}) one can calculate the density expected for this d.s.c. level of crystallinity, namely ρ. From ρ and ρ_d one can estimate the volume per cent microvoids formed as a function of draw rate (*Table 1*). These data show a change in slope or discontinuity between $R_d = 10$ and 25 cm min^{-1}.

The effect of draw rate on the natural draw ratio (λ_n) of polypropylene is shown in *Figure 9*. The natural draw ratio is essentially constant over the range 0.5–5 cm min^{-1}. When draw rate is larger than 10 cm min^{-1}, the natural draw ratio increases rapidly and is presumably associated with void formation. *Figure 10* shows that the yield strain of polypropylene is also dependent on draw rate. However, unlike the many other parameters determined, yield strain shows a continuous slight increase as draw rate increases until $R_d > 50$ cm min^{-1}. It is only above this rate that one sees a more rapid increase in yield strain.

Figure 11 shows the effect of draw rate on the stress to break for polypropylene. It is clear that there is a maximum value of the stress to break near $R_d = 10$ cm min^{-1}. When the draw rate is larger than 10 cm min^{-1} the stress to break for polypropylene decreases with increasing draw rate.

Figure 12 shows the changes that occur in the

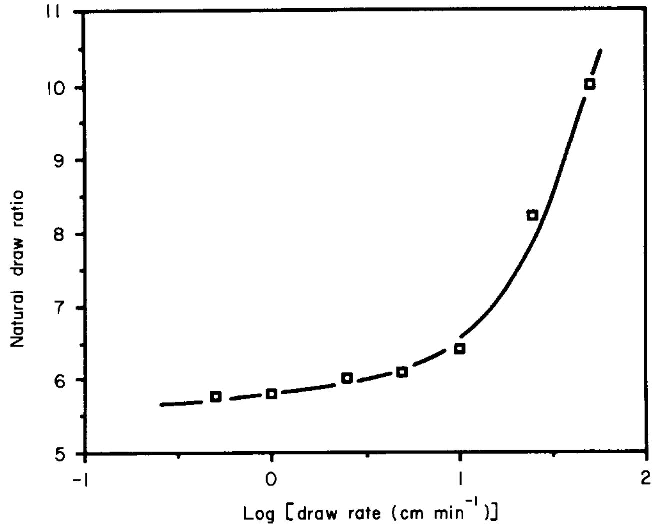

Figure 9 The effect of draw rate on the natural draw ratio of polypropylene

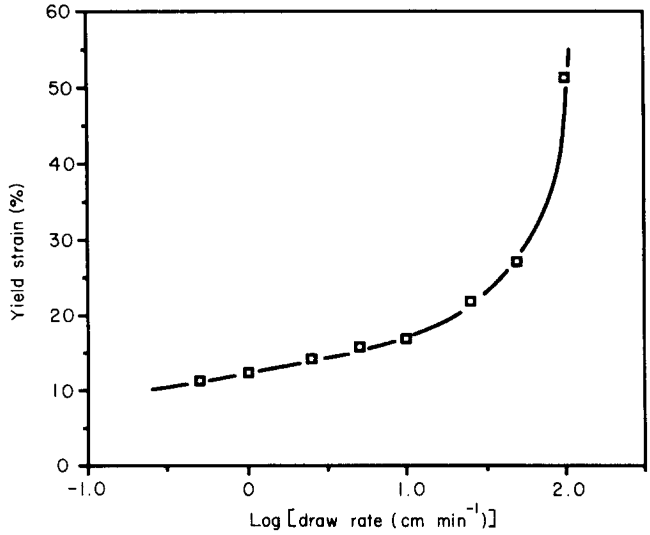

Figure 10 The effect of draw rate on the yield strain of polypropylene

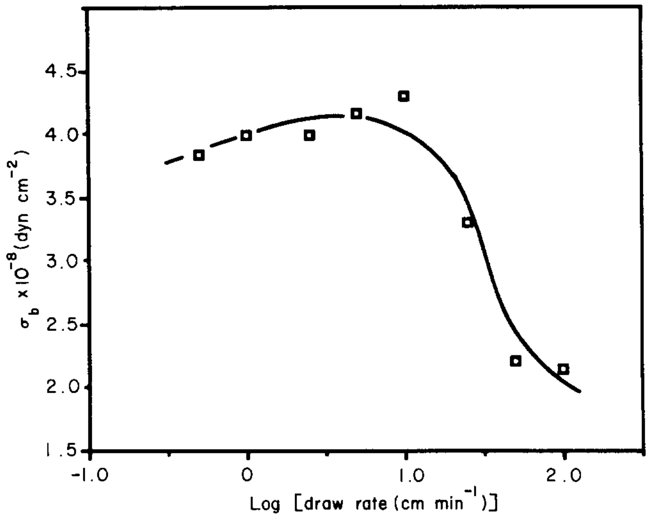

Figure 11 The effect of draw rate on the stress to break (W_b) of polypropylene

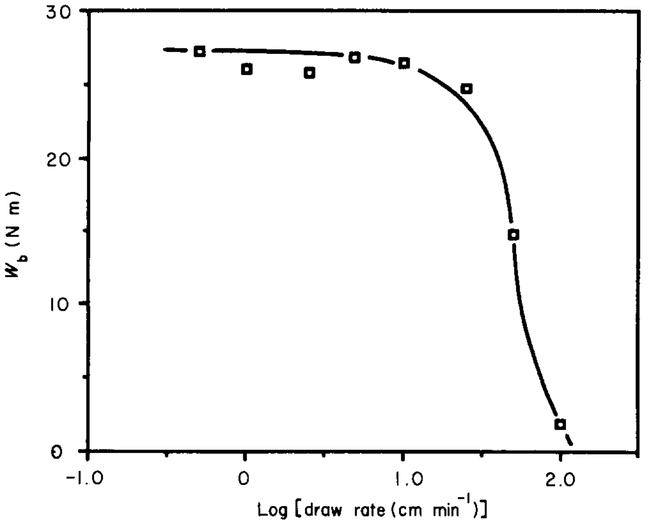

Figure 12 The effect of draw rate on the work to break for polypropylene

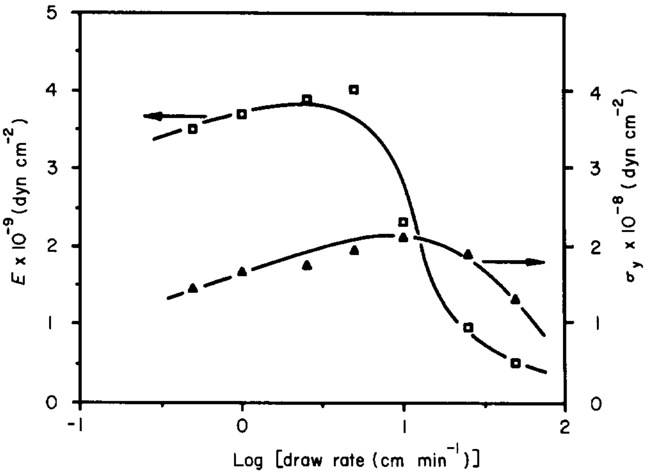

Figure 14 The effect of draw rate on the modulus (□) and the yield stress (▲) of high-density polyethylene

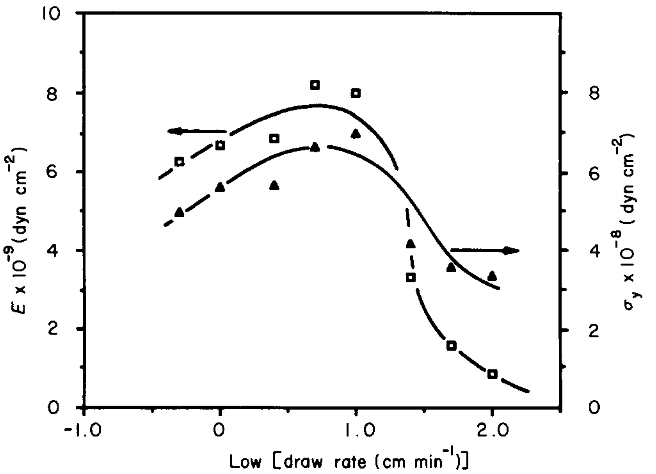

Figure 13 The effect of draw rate on the modulus (□) and the yield stress (▲) of poly(ethylene terephthalate)

toughness of polypropylene as draw rate is increased. The orginate (W_b) is the area under a stress–strain curve. At $R_d < 10\,\mathrm{cm\,min^{-1}}$ the toughness of polypropylene is effectively independent of draw rate. In contrast at $R_d > 10\,\mathrm{cm\,min^{-1}}$ the toughness of polypropylene decreases rapidly as draw rate increases.

On the basis of the above experimental results, it can be concluded that the yield mechanism of polypropylene changes dramatically with draw rate. When the draw rate is less than $10\,\mathrm{cm\,min^{-1}}$ chain slippage before yield dominates, so the density of the sample before yield shows little variation. However, at $R_d > 10\,\mathrm{cm\,min^{-1}}$ void formation before yield dominates, and the tensile properties of polypropylene are apparently largely determined by flaws, microvoids and the propagation of these entities. As a result, both modulus and yield stress decrease as draw rate increases above this critical level. The time–temperature superposition principle no longer appears to hold under these conditions.

In earlier work[2,3,6] concerned with the effect of draw rate on modulus and yield stress of a polymer, the maximum draw rate used was typically $5\,\mathrm{cm\,min^{-1}}$. Nevertheless, in at least one case, a study of the cold drawing of poly(ethylene terephthalate)[11], the maximum draw rate used reached $50\,\mathrm{cm\,min^{-1}}$. However, although drawing stresses were reported, the yield stress data at $R_d > 10\,\mathrm{cm\,min^{-1}}$ were not given.

It is not just polypropylene that shows a modulus and yield stress decrease when draw rate is larger than a critical value. The same phenomenon has also been observed in poly(ethylene terephthalate) and high-density polyethylene. *Figure 13* shows modulus and yield stress values for poly(ethylene terephthalate) as a function of draw rate from 0.5 to $100\,\mathrm{cm\,min^{-1}}$. It is clear that when $R_d > 10\,\mathrm{cm\,min^{-1}}$ both modulus and yield stress decrease rapidly as draw rate increases. *Figure 14* shows similar plots for high-density polyethylene; once again a decrease in modulus and yield stress is observed, in this case at slightly different values of draw rate.

Clearly there is a critical draw rate for polymers; when draw rate is larger than this critical value, modulus and yield stress decrease as the draw rate increases. The critical draw rate for various other grades of polypropylene, poly(ethylene terephthalate) and high-density polyethylene that have been examined, but are not reported here, varies between 5 and $25\,\mathrm{cm\,min^{-1}}$. Discovery of this phenomenon is, potentially, of considerable practical importance in the processing of these materials.

CONCLUSIONS

Young's modulus, yield stress and other parameters associated with the drawing response of certain polymers (polypropylene, poly(ethylene terephthalate) and high-density polyethylene) are greatly decreased when the draw rate is larger than a critical value. This is caused by a change in the yield mechanism as draw rate increases. At high draw rates void formation dominates and the tensile properties of the polymer are largely determined by flaws and submicroscopic cracks.

During cold drawing of a polymer, the neck-forming process is different from the neck-propagating process. The mechanism of the start of the neck formation does not involve a temperature rise. However, once the neck has formed, its propagation can be affected by subsequent temperature changes.

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