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Polymer 42 (2001) 9301–9312

polymer

www.elsevier.com/locate/polymer

Adiabatic failure in polyethylene

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Received 17 January 2001; received in revised form 15 May 2001; accepted 5 June 2001

Abstract

A series of true stress–strain curves measured in tension, published by Hiss and Strobl [Deformation, yield and fracture of polymers (1997) 439], have been modelled using a Gaussian equation to represent strain hardening. An empirically-based constitutive relation was extracted from the data spanning the temperature range 24–128°C. In the first procedure, adiabatic heating was introduced into the constitutive relation at constant true strain rate by means of an explicit integration scheme that equates incremental plastic work to a temperature rise. At the end of each increment the material properties were adjusted to account for the increase in temperature. In the second procedure, a constant load was assumed and the temperature rise was calculated directly from the work done together with a curve relating temperature to energy input. In each case, it was found that adiabatic conditions had a destabilising effect, which was interpreted using the Vincent–Considere criteria. The possibility of using draw stress instead of yield stress in the calculations was considered and it was concluded that such a change would not qualitatively affect the results.

The rise in deformation stresses and the reduction in specific heat at low initial temperatures is expected to increase the thermomechanical instabiliy.

These conclusions were shown to be insensitive to minor changes in crystallinity during deformation.

Keywords: Tensile stress; Strain rate; Adiabatic

1. Introduction

Previously, Vincent [1,2] put forward a number of generalities in relation to the deformation and failure of thermoplastics. In order for necking to take place, the true stress–strain curve must show a tangent from the origin in accordance with the first Considere condition but for the necking to be stable with fresh material being drawn in from the undeformed part of the test piece, there had to be a second tangent which corresponded to the point where the nominal stress started to increase. Although this is a necessary condition it has not been shown to be generally sufficient, especially when the tangent occurs at a relatively low nominal stress. In a second paper [2], Vincent suggested that when the deformation of a polymer under tension did not meet the second condition and occurred at a steadily falling nominal stress, the fracture was to be expected. To support this proposition he studied the deformation and necking of PVC, and was able to estimate the approximate form of a true stress–strain curve from the neck shape and nominal stress. After deriving a series of such curves at different temperatures he concluded that adiabatic deformation would indeed lead to a continuously declining nominal stress. Later, Cross and Haward [3] reached similar conclusions and showed that when a PVC test piece was lengthened to give a spring like attachment beyond the dumbbell, the deformation process became adiabatic, and a relatively brittle fracture was observed at the initiation of the necking process. At the same time an increase of some 24°C was measured at the fracture surface by means of infrared photography. It should also be noted that the provision of sufficient reversible elastic energy in the test piece to complete the adiabatic fracture was in this case an essential feature of the brittle behaviour. With a conventional short dumbbell test piece normal necking took place.

Until recently, further estimation of adiabatic effects was limited by the absence of both quantitative true stress–strain measurements and a theoretical treatment suitable for the interpolation and extrapolation of the results. However, new techniques have now been developed which make it possible to derive true stress–strain curves by measuring the deformation at the waist of an hour glass test piece. Results have been reported with a number of thermoplastics by G'Sell and Jonas [4,5], Hope Ward and Gibson [6], and Hiss and Strobl [7].

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PII: S0032-3861(01)00447-5

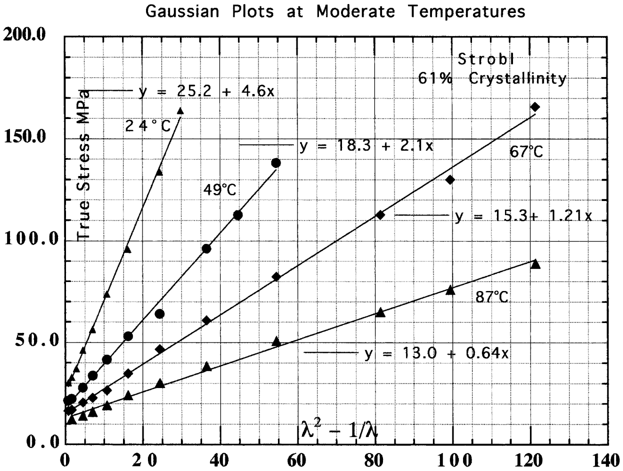

Fig. 1. Gaussian plots are fitted to the points taken from Hiss and Strobl's true stress–strain curves in the temperature range 24–87°C. It should be noted the Gaussian straight lines are defined by two constants, the extrapolated yield stress and the strain hardening constant *Gp*. The lines fit the measurements well up to λ values of 5 at low temperatures and up to 10 at higher temperatures.

Further it has been found possible to model the post-yield deformation process by making use of the hypothesis proposed by Haward and Thackray [8]. The model proposes that the stresses required for large post-yield deformations with thermoplastics may be treated as a combination of a viscous resistance and an entropic, rubber–elastic stress acting in parallel. In the original paper the rubber elasticity forces were treated according to the non-Gaussian statistics described by Treloar [9] but since that time it has been shown in several publications [5,10–12] that in many cases, and especially with polyethylene, the simple Gaussian relation is satisfactory. The two treatments are, of course, closely related. The Gaussian equation has the form shown below.

True stress (at constant true strain rate) = σ_{true}

$$= Y + Gp(\lambda^2 - 1/\lambda) \tag{1}$$

where *Y* is an extrapolated yield stress, *Gp* the strain hardening constant and λ the extension ratio. Experimentally it was also found that both *Y* and *Gp* varied with strain rate and temperature and were capable of being represented by Eyring type processes [12].

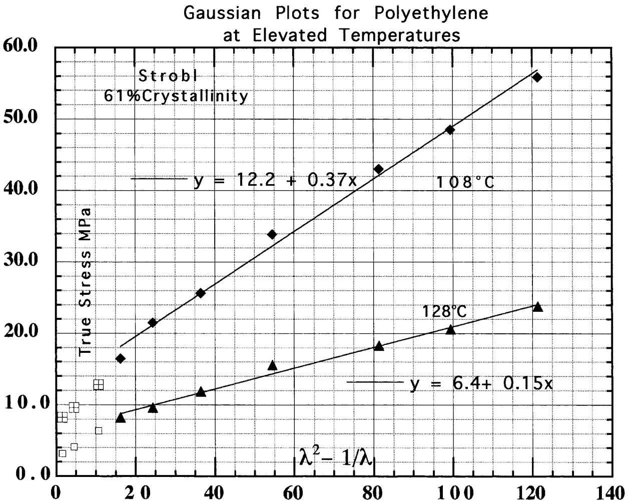

Fig. 2. As in Fig. 1 but for temperatures 108 and 128°C. Note the deviation of experimental points from the Gaussian line at each end of the curves. Only the central part of the curves need to be used in the calculations.

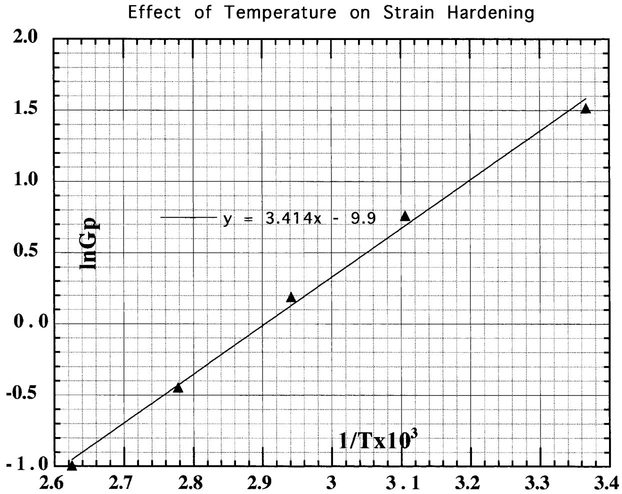

Fig. 3. The relation of the Gaussian strain hardening parameter, *Gp* to temperature.

2. The application of the results of Hiss and Strobl

In this paper, we start from the work of Hiss and Strobl [7] in which true stress–strain curves were measured for a polyethylene with 61% crystallinity over a wide range of temperatures at a strain rate of 10^{-2} s^{-1}. The original curves have already been published [7,12]. They provide a group of measurements over a range of temperatures essentially analogous to those used by early workers to predict adiabatic stress–strain curves [2,13]. However, because the true stress–strain curves are well represented by Gaussian plots they are more suitable for quantitative treatment and their use for adiabatic calculations also benefits from the availability of thermodynamic data as described in Appendix A. In Figs. 1 and 2 Gaussian lines give a good fit to the points taken from Hiss and Strobl's curves. In Figs. 3 and 4 the parameters of the Gaussian lines are plotted against reciprocal temperature. Bringing all these results together makes it possible to derive Eq. (2a) for the nominal stress.

$$\sigma_n = \left\{ \frac{19,300/T - 40.6}{\lambda} \right\} + \exp(3414/T - 9.9)(\lambda - 1/\lambda^2) \tag{2a}$$

and the true stress

$$\sigma_\tau = \sigma_n \lambda \tag{2b}$$

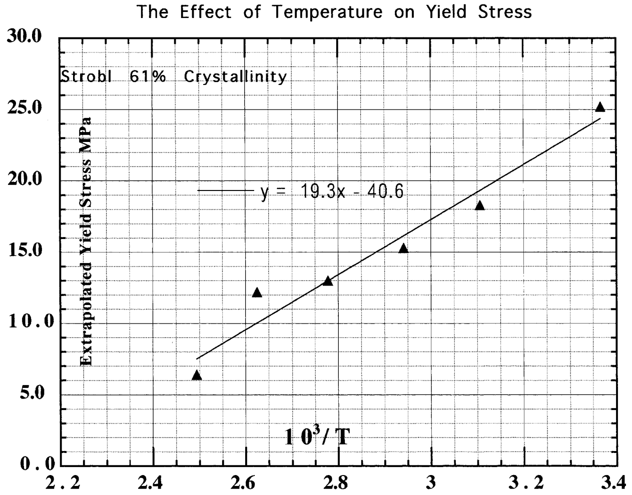

Fig. 4. The relation of the extrapolated yield stress to temperature.

This gives the nominal stress for a section of material extended to a particular value of λ at the prescribed strain rate and temperature. It embodies the results of Hiss and Strobl [7] in the simplest possible way and makes no attempt, to incorporate them in the format of conventional Eyring equations. Their validity over a range of extension ratios corresponds with that of the Gaussian lines in Figs. 1 and 2, i.e. up to values of 5 at 24°C and up to 11 at higher temperatures. It is also assumed, unavoidably, that stresses calculated in this way are unaffected by the pathway by which they were reached.

3. Procedures and materials

The main work described in this paper was based on a series of true stress–strain curves measured at six different temperatures by Hiss and Strobl [7] which were later reproduced in Ref. [12]. The temperatures used were those quoted in Figs. 1 and 2 and the strain rate was $10^{-2}\,\mathrm{s}^{-1}$. The material was supplied by BASF and had a crystallinity of 61%, a molecular weight (M_w) of 390,000 and a polydispersity of 6.5.

One set of calculations was made with a series of polyethylenes of differing crystallinity, also measured by Hiss and Strobl [7]. In this case the three materials of lowest crystallinity were ethylene vinyl acetate copolymers.

In treating the results, points were taken from the experimental curves either with a scanner or from enlarged photocopies.

The calculations described here deal almost exclusively with post-yield deformation. The polymer studied shows a pre-yield strain of around 10% ($\lambda = 1.1$) which is neglected. In fact this deformation is a complex process involving a reversible Hookean component and mainly reversible viscoelastic strains. The Hookean component entails a fall in temperature according to the Joule–Thompson equation [14] first shown to apply to plastics by McNally and Shepherd [15] while plastic deformation acts in the opposite sense. From the aggregate thermal effects point of view the neglect of low strains is therefore unlikely to cause serious error. A recent study of pre-yield deformation has supported the concept of two distinct processes [16].

Scanning electron microscopy was carried out on notched charpy test pieces broken at room temperature under impact at $1\ \mathrm{m\,s^{-1}}$. The polymer had a molecular weight (M_w) of 185,000, a density of 0.94 with 4.5 branches per 1000 C atoms. The samples were prepared by S. Hasra (Imperial College [17]) and SEMs were taken by Hasra and I Brough (Manchester University Material Science Centre).

4. The application of adiabatic conditions to true stress–strain curves

In this section adiabatic conditions are introduced as a modification of the experimental results reported by Hiss and Strobl. In an actual experiment, of course, adiabatic conditions would not prevail at the strain rates used. However, as a first step in a study aimed at the prediction of adiabatic effects, it was considered desirable to demonstrate the way in which adiabatic heating alone could change a true stress–strain curve under the exact conditions in which it was measured. Thus, the product of the present calculation is a true stress–strain curve at constant true strain rate $\{(\mathrm{d}\lambda/\mathrm{d}t)/\lambda\}$ under conditions where all ($\beta = 1$) or half ($\beta = 0.5$) of the work done is converted into measurable heat. It may be noted that recent studies on adiabatic extrusion have given β values of 0.90 and above (see Appendix A.5).

From this calculated adiabatic curve, a true nominal stress relation can be derived for deformation at a constant true strain rate. This represents the form, which a conventional test would take if uniform deformation occurred and the rate of extension was controlled to maintain a constant true strain rate.

The conversion from an isothermal to an adiabatic relation is done simply by introducing the heating factor according to the equation:

$$\mathrm{d}T/\mathrm{d}\lambda = \left\{ \frac{\beta\sigma_t}{\lambda\rho C_p} \right\}$$

where T is the absolute temperature, ρ the density and C_p the specific heat. The thermomechanical conversion ratio β represents the proportion of the work done which appears as measurable heat. It is assumed to be unity unless otherwise stated. Together with Eqs. (2a) and (b) this equation may be numerically integrated to give a calculated adiabatic true stress–strain curve as defined above.

In Fig. 5a the original true stress–strain curve at 24°C is plotted side by side with Fig. 5b where two adiabatic curves are plotted in a manner suitable for applying the Considere construction. It will be seen that, under adiabatic conditions,

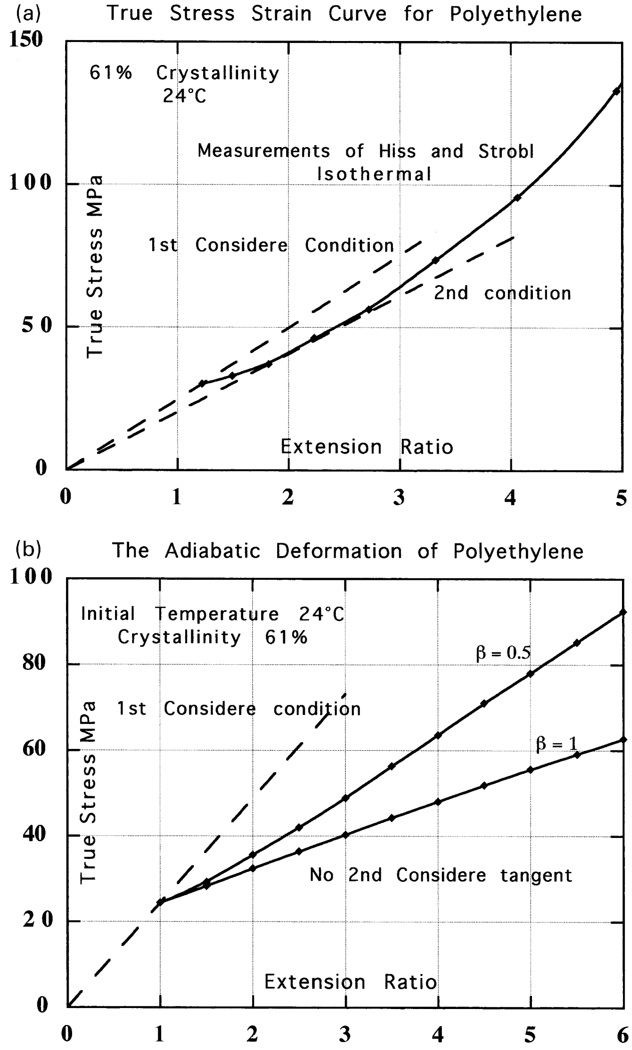

Fig. 5. (a) The main high strain part of the 24°C isothermal true stress–strain curve from Hiss and Strobl showing its compliance with both Considere conditions for stable necking. (b) Calculated adiabatic plots with a starting temperature of 24°C using two values of β, the thermomechanical efficiency constant. Neither curve has a second Considere tangent.

even with a β value of 0.5 there is no second tangent as required for the stable extension of a neck. So the nominal stress falls continuously with increasing extension ratio as shown in the top curve of Fig. 6.

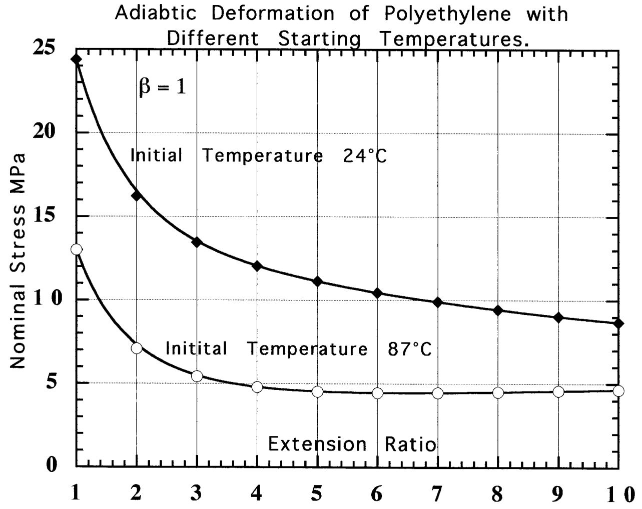

Fig. 6. Nominal stress–strain curves for adiabatic deformation at two starting temperatures. The 24°C curve shows a continuous fall in stress. The 87°C curve shows a slight rise in stress above $\lambda = 6$ showing local stabilisation of the deformation process but there is no indication that σ_n could rise above its initial value and so drag more material into the extension process.

As far as is known, with the possible exception of low molecular weight materials, the true stress–strain curves of all commercial polyethylene thermoplastics are consistent with stable necking in a conventional tensile test at low strain rates, e.g. Coates and Ward [18], Haward [19]. The reason for the predicted departure from compliance under adiabatic conditions is, of course, the softening effect due to the rise in temperature. The estimated temperature changes in the present cases are presented in Fig. 7 which are based on the experimental curves at 24 and 87°C. In all cases there is an increase in temperature with extension ratio but the increase is much greater at the lower temperature than at 87°C. This relates directly to Eq. (2a) and to the scaling factor represented by the ratio of stress to specific heat $\sigma_{\text{true}}/\rho C_p$. Although the fall in the stresses required for deformation at higher temperatures is common to all thermoplastics, we may note that in our treatment they are related to the quantities Y and $1/C_p$, both of which fall at higher temperatures in a similar way . As values for C_p over a wide range of temperatures are not generally available, an indication of the effect of temperature on the scaling factor for high crystalline polyethylenes in terms of the ratio $Y/\rho C_p$. is given in Fig. 8 . Here the yield stress measurements were taken from Brooks, Duckett and Ward [20], the thermodynamic constants from Gaur and Wunderlich [21]

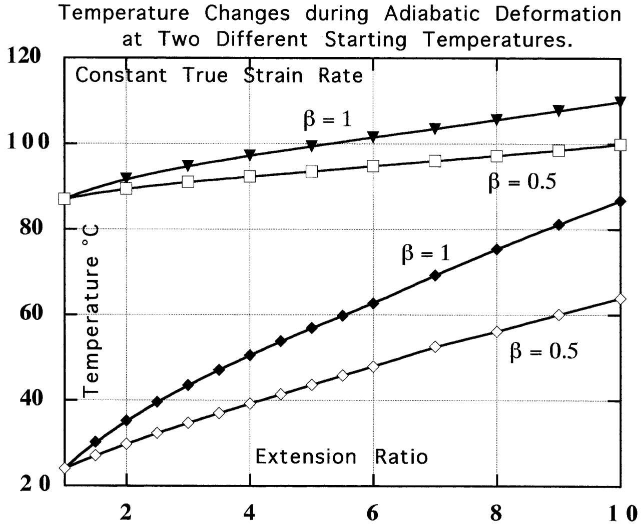

Fig. 7. Temperature changes during the adiabatic deformation of true stress–strain curves. Note the larger temperature changes at lower starting temperatures.

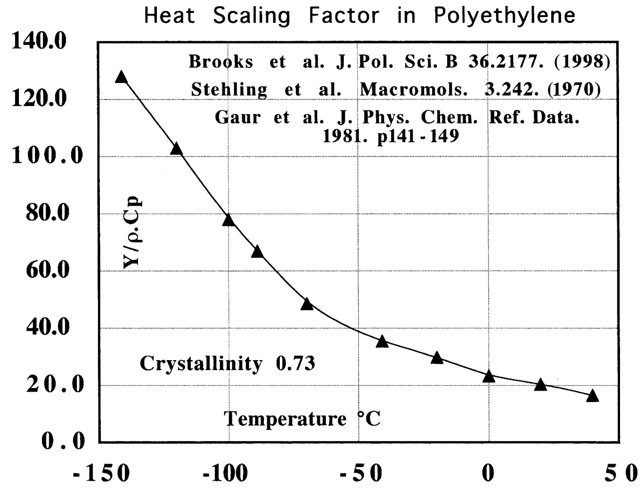

Fig. 8. The scaling factor $Y/C_p\rho$ determines the magnitude of the heating effects in adiabatic deformations under a constant nominal stress. Data from the references shown.

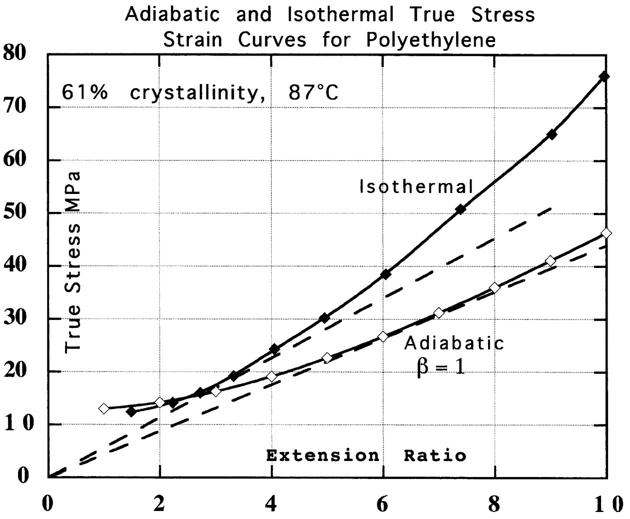

Fig. 9. Adiabatic and Isothermal true stress–strain curves starting at 87°C. The adiabatic curve just manages to meet the second Considere condition. (see Fig. 6).

and density temperature relations from the work of Stehling and Mandelkern [22]. (see Appendix A.1). Thus, a strong sensitivity to the starting temperature of the polymer is a fundamental feature of the adiabatic heating process. This is also in line with the conclusions of Ritchie Davis and Leevers [23].

This point is further shown in Fig. 9 where it is shown that at 87°C, even with a β value of 1, the adiabatic true stress–strain curve still meets the second Considere condition. The equivalent true nominal stress–strain curve has been included in Fig. 6 where it will be seen that there is a very small rise in stress at high strains. As already pointed out, in order for stable drawing to take place it is necessary to meet the second Considere condition, as proposed by Vincent [1]. However, examination of Figs. 6 and 9, along with more general considerations, indicates that this may not, by itself be a sufficient criterion. It seems most unlikely that the nominal stress measured at 87°C, in the bottom curve in Fig. 6 will ever approach either the level of the initial yield stress or the estimated draw stress (7.2 MPa), and so enable more material to enter the neck. However there is a long flat section, above extension ratios of about 5, where the temperature exceeds 100°C, and where locally stable extension would be expected. In the ensuing discussion it will be suggested that this condition defines the lowest limiting temperature for high speed melt spinning processes [24] and for the extension of long filaments in the final stages of fracture.

5. Deformation under constant nominal stress

5.1. Deformation during fracture

In Section 4 it has been shown that adiabatic heating is quite capable of softening a polyethylene in such a way that true stress–strain curves would be unstable in terms of the requirements of a conventional test. However, there are no present measurements of true stress–strain curves under adiabatic conditions and the recording of such measurements in the future may well be problematic. In a conventional test at a constant rate of extension, the large strain process is initiated at the yield stress after which a neck is formed which in the presence of triaxial forces generated by the neck [25], can propagate into undeformed polymer at a stress below the yield stress, generally known as the draw stress. Within the neck there are very large variations in strain rate, as shown by Coates and Ward [18] and other workers [19,26]. In the ensuing treatment a yield stress is used having the lowest value consistent with Hiss and Strobl's results (see below).

Another possibility would be to base the calculation on the draw stress, which according to measurements of Andrews and Ward [27] comes to 65% of the yield stress (24 MPa). However, higher values of up to 80% are quoted for other high-density polyethylenes. The value based on the lower ratio will be shown on the figures given below. However, it is not possible to calculate a draw stress from such results as those of Hiss and Strobl. In Appendix A an attempt is made to estimate the yield stress which would be measured in a conventional test, leading to a 65% draw stress of 19.5 MPa. Recalculation of our results at 24°C, based on this figure gives results qualitatively similar to those presented here. (see Appendix A.4).

However, most significant fracture processes occur, not as an instability in a bulk deformation process but within a highly constrained volume at the head of a crack. With glassy polymers Kramer [28], Donald [29] and Lauterwasser [30] and coworkers, have developed a comprehensive theory according to which a crack leads into a craze which is stabilised by fibrils drawn out from the matrix surfaces. In

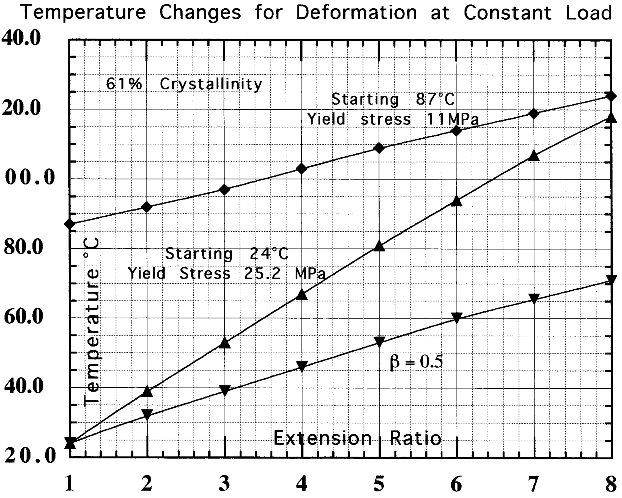

Fig. 10. The lines plotted show the predicted temperature rise for tensile deformation at constant nominal stress. This rise is also reduced at the higher starting temperature.

this process the amount of energy absorbed depends on the ability of a craze fibril, after extension to its limit, to draw in fresh material from the bulk phase under the influence of a constant nominal fibre stress. Under fast or brittle fracture conditions there is evidence of raised temperatures and melting of the fibrils [31–33].

Both the practical and theoretical study of fracture processes has been developed through the discipline of fracture mechanics. This is concerned with the absorption of energy through constrained plastic deformation zones ahead of a crack. Such layers, sometimes described as Dugdale zones, may consist of a craze or of a more chaotic deformed layer often containing crazed elements. They are formed when, as in a craze, material is dragged into the plastic zone by tensile stresses perpendicular to the direction of crack growth. Clearly in a fast process measurable heat will accumulate in the plastic zone leading to an increase in temperature, which will be greatest when the rate of deformation exceeds the speed at which the heat is dispersed by conductivity. The accumulation of heat in a plastic zone in front of a crack has been recently reported by Karger-Kocsis and Moskala [34] at quite modest speeds, while Leevers [35–37] has argued that the toughness of plastics under impact loading or at high speeds is determined by the competition between thermomechanical heating and thermal conduction and at high speeds toughness is reduced by thermal decohesion in a Dugdale zone [35]. This is in line with earlier work by Williams [38] and Doll [39,40] on the fracture of polymethyl methacrylate who found that the energy required for crack propagation was reduced at high crack speeds.

Thus, in some respects the plastic deformation and crazing at the tip of a crack mimics on a microscopic scale the cold drawing in bulk tensile specimens and refocuses interest on the stability of bulk drawing at rates where adiabatic heating becomes important. In Section 5.2 the adiabatic extension of a section of a polymer test piece under a constant nominal stress will be evaluated.

5.2. Adiabatic extension under a constant nominal stress

When a force is applied to one end of a test piece deformation within the sample must take place under conditions of constant nominal stress or load along the length of the test piece. For present purposes the two undeformed or matrix ends of a deforming polymer sample are considered to be subject to its yield stress Y which provides the constant load deforming the material in between. At this stress it is assumed that more material can be drawn in from the undeformed part of the test piece or from the surface of the matrix surrounding a craze at deformation zone. The way this stress is estimated is of some importance as its value largely determines the amount of adiabatic heating. In the first calculation at 24°C (Fig. 11 below), the yield stress was extrapolated to zero strain in accordance with Eq. (1). However at 87°C the Gaussian plots at low strains gave stresses higher than the measured values (Fig. 1) and the value of Y was taken directly from the measured curves.

Using the yield stress as described above the work done on a section of polymer extended to any ratio λ is then simply $Y(\lambda - 1)\,\mathrm{MJ\,m^{-3}}$ and the rise in temperature is given by:

$$\frac{(\beta Y(\lambda - 1))}{C_p\rho}$$

From the above it is clear that, as with the previous case the magnitude of the thermal effect will be dominated by the scaling factor $Y/C_p\rho$ (Fig. 8), so that the calculated amount of adiabatic heating increases very strongly as the starting temperature is reduced.

In order to estimate the temperature reached after deformation under a constant nominal stress, a relation between heat content and temperature is required. This was obtained from the data of Gaur and Wunderlich [19] as shown in Appendix A.2. The increase in temperature due to the deformation is then obtained by adding in the energy in Joules given by $Y(\lambda - 1)$ and introducing the appropriate value for β. These results are given in Fig. 10. Comparison with Fig. 7 also shows that the adiabatic effects with the constant load system are greater than when a constant true strain rate is employed.

5.3. Comparison of adiabatic and isothermal deformation at constant load

Once we know the temperature at any given extension ratio we can calculate the stress according to Eq. (2a) and (b). Although this may easily be done it is very important to consider the nature of the stress, which is estimated in this way. In fact this may be defined quite precisely. Eq. (2a) simply generalises the measurements shown in Figs. 1 and 2 and fills in the intermediate data. Thus it refers to

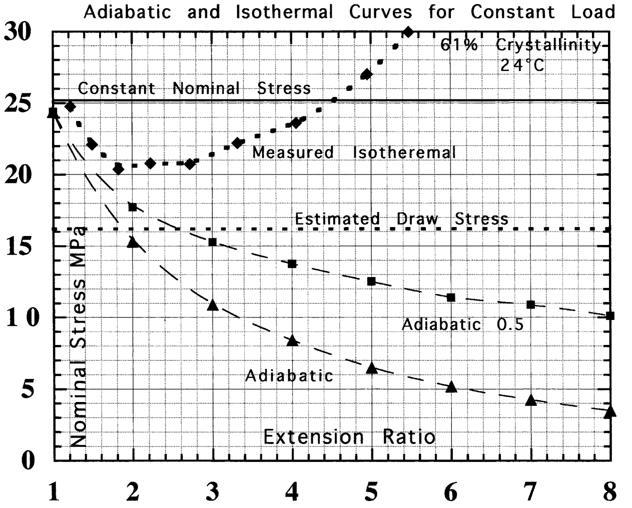

Fig. 11. Measured curves and adiabatic curves calculated for a constant nominal stress. The isothermal curve rises to cut the yield stress but both the adiabatic curves fall continuously. All the curves represent the nominal stress at the relevant temperature for a constant true strain rate at the temperature reached (Fig. 10). In a real experiment very large increases in the rate of strain are required to meet the condition of constant nominal stress. This may lead to failure. The draw stress has been drawn at 65% of the yield stress [27].

experiments at different temperatures all made at a constant true strain rate of 10^{-2} $\mathrm{s}^{-1.}$ However, the temperatures now applied are those which have been estimated to prevail in a system under constant nominal stress represented by the top flat line in Figs. 11 and 12. In real experiments at constant nominal stress the difference in stress between the top flat line and that represented by the curves would be compensated by a difference in strain rate and where the differences in stress are large the strain rates would have to increase by one or more orders of magnitude (see Refs. [18,19,26]). It seems reasonable to conclude that such a process could not continue indefinitely, at some point, if the gap between the stresses became too large fracture would intervene. It is proposed that this process may be regarded as a more detailed description of the hypothesis put forward by Vincent [2]. The results of the calculations are compared with isothermal curves for the measured nominal stresses at different extension ratios in Figs. 11 and 12. It will be seen that at 24°C, and even when a β value of 0.5 is employed, the stress at constant strain rate falls continuously so that, according to Vincent's hypothesis, fracture is indicated. It should also be noted that the stresses estimated under adiabatic conditions never reach the postulated draw stress.

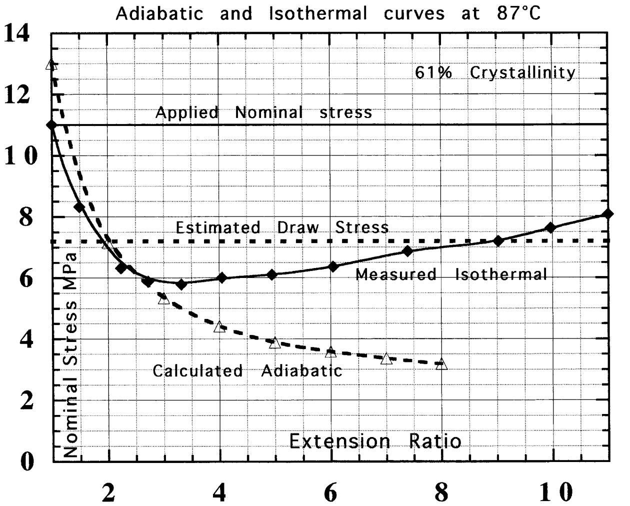

Fig. 12. Measured isothermal and calculated adiabatic ($\beta = 1$) curves for a starting temperature of 87°C. Under these conditions the calculated stress falls continuously (compare Fig. 6). At high strains the 65% draw stress is exceeded under isothermal but not under adiabatic conditions.

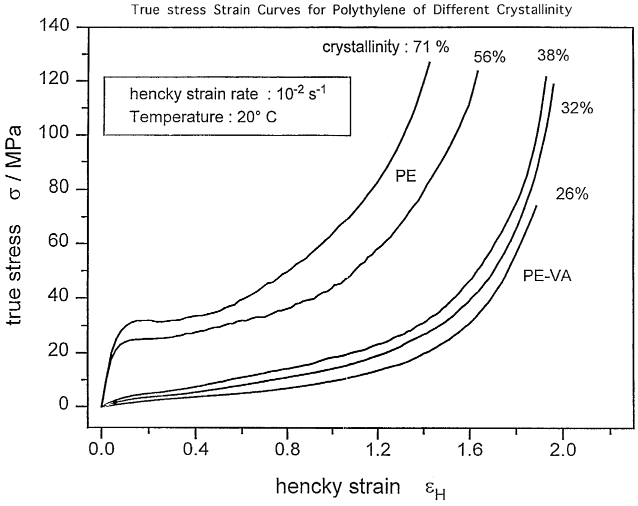

Fig. 13. True stress–strain curves as measured by Hiss and Strobl for polyethylenes of different crystallinity.

5.4. The influence of crystallinity

If changes in crystallinity take place during the deformation, as has been reported (for example by Meinel and Peterlin [41]), energy will be absorbed by melting or released by crystallisation. In each case there will also be changes in mechanical properties, with melting making the polymer softer and crystallisation the reverse. The possibility of crystallinity changes clearly complicates the calculation of heating effects in the adiabatic deformation of semi-crystalline polymers such as polyethylene. However the simplifications arising from the constant load assumption make it possible to compare the softening effects due to a rising temperature with those associated with an isothermal reduction in crystallinity. For this purpose use is made of a second series of true stress–strain curves measured by Hiss and Strobl [7]) using polyethylene copolymers with different proportions of crystalline material as shown in Fig. 13. These curves also give good Gaussian plots up to moderate strains, which will not be detailed here, as it does not form a part of the present investigation. However, the extrapolated yield stress of

25 MPa for the 71% crystalline material was taken from the Gaussian plot. Using this figure for Y it is possible to estimate the proportion of crystal which would be melted if all the work done was applied in this way as in the equation below.

$$\text{work applied} = Y(l - 1) = \rho f_c(0.71 - c)$$

where f_c is the heat of fusion (243 J g^{-1} [21]) and c is the proportion of crystallinity. The levels of crystallinity may then be estimated as a function of the extension ratio and the appropriate stress read off from the curves shown in Fig. 13 for each of the crystallinities presented. The value of the stress at a strain rate of $10^{-2}\,\text{s}^{-1}$, would then be that expected as the result of the proposed process. This could then be compared with that derived from the previous adiabatic assumption at constant crystallinity as shown in Fig. 14. Unexpectedly the two lines are rather close together. Although the estimates are only approximations, it is nevertheless concluded that if some of the energy in a presumed adiabatic deformation was consumed in melting crystals the resulting differences in estimated stress would not be so large as to invalidate the adiabatic calculations described in Section 4 of this paper.

6. Discussion

It will be clear from the above examples that if adiabatic deformation occurs at stresses associated with the deformation of high density polyethylenes, then the resulting heating effect will reduce the stresses required for deformation and promote plastic instability. The question therefore arises as to whether adiabatic heating actually occurs in practical experiments, especially under fast fracture or impact conditions.

There are three factors which might be expected to influence this situation. Firstly the effect of strain rate on the stresses required for deformation, secondly the possible effect of internal energy on the formation of measurable heat and thirdly whether the conditions envisaged in the theory have been shown to give measurable heating in actual experiments.

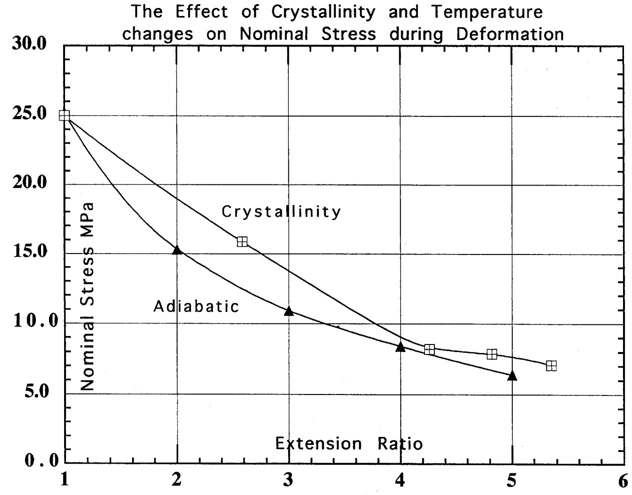

Fig. 14. The adiabatic curve taken from Fig. 11, compared with an isothermal curve derived from Fig. 13 where all the work done was assumed to melt crystals.

6.1. The influence of strain rate on yield stress

As already noted, the present calculations for thermomechanical heating are based on stresses at strain rates of $10^{-2}\,\text{s}^{-1}$, while adiabatic conditions are expected only at much higher strain rates e.g. $10^{2} - 10^{3}\,\text{s}^{-1}$. It is known that the stresses required for the deformation of high-density polyethylene is affected by changes in strain rate and there are a number of measurements of this effect (see Appendix A.3). In particular, the compression measurements of Walley and Field [42] comprise very high strain rates and reported values for the yield stress of 20.0 at $10^{-2}\,\text{s}^{-1}$, 37.2 MPa at $10^{2}\,\text{s}^{-1}$ and 41.6 MPa at $10^{3}\,\text{s}^{-1}$. From this it may be concluded that yield stress increases by a factor of about 2 over the relevant range of strain rates. This would lead to an equivalent increase in thermal effects during fast facture.

Higher stresses may also have the effect of restricting the size of a deformation zone through viscoelastic effects or through the increased localisation of strain under conditions of plastic instability.

6.2. Internal energy changes

When large deformations take place with carbon chain polymers such as polyethylene, the distortion of the molecular coil also requires changes in the proportions of rotational isomers. A polyethylene macromolecule has been modelled using simulation procedures by Mckechnie et al. [43] who showed that when the extension ratio is increased up to a value of 1.5 there is an associated increase of about 5% in the proportion of trans isomers. Since these represent a lower energy state than the gauche configurations there should be an increase in the heat given out.

Similarly when an unperturbed polyethylene chain is in a rubbery state above its crystal melting point, an increase in temperature leads to a decrease in its end-to-end distance and hence to differences in the rubber elastic stresses when deformed. These have been studied by Ciferri, Hoeve and Flory [44,45] and their work has been summarised in Ref. [9] and more recently by Erman and Mark [46]. The latter reported that the difference amounted to an increase of some 30–40% in the heat generated by the change in entropy due to changes in chain conformation.

If this principle applies to the thermal effects estimated here it would significantly increase the heating effect associated with the strain hardening (entropic) part of the deformation process.

Recent research by Robertson, Klein, Ward and Packers [47] has concluded that the internal energy changes may be greater than those previously reported.

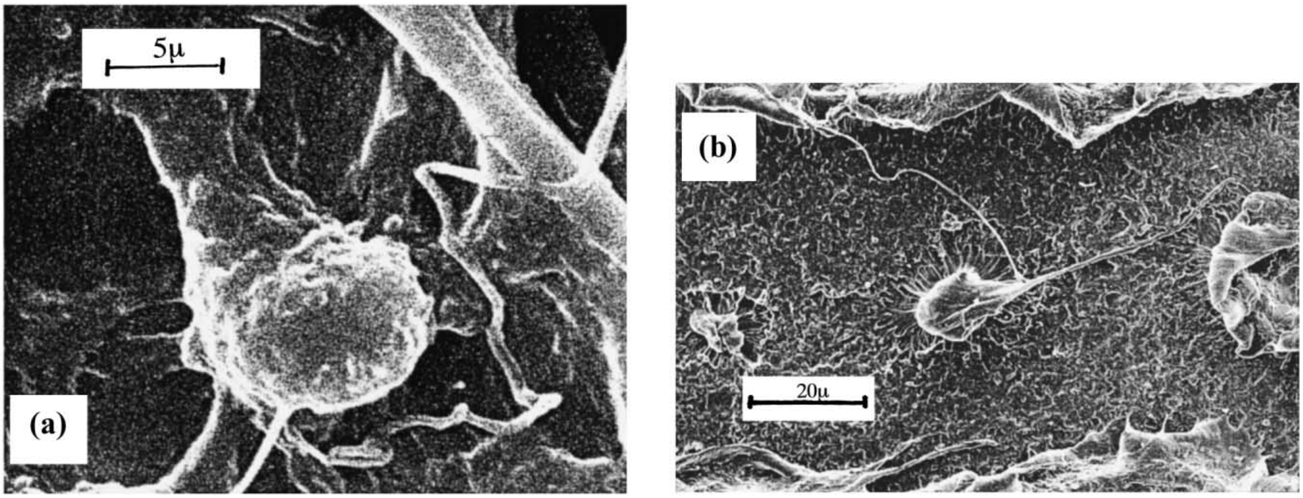

Fig. 15. Scanning electron micrographs of polyethylene fracture surfaces showing highly drawn fibres [17]. Prepared as described in Section 3, (a) Showing a worm like feature believed to have been formed by the retraction while hot of a broken long fibril. (Photo S. Hasra [17]). (b) A long drawn fibre originating in a zone of high deformation. (Photo I. Brough [52]).

6.3. The transition from isothermal to adiabatic deformation

In their work on the cold drawing of polyethylene (yield stress 26 MPa at 10^{-2} s^{-1}), Andrews and Ward [27] varied strain rate over a wide range and observed changes in stress and draw ratio. At strain rates above $\sim 8 \times 10^{-3}$ s^{-1} the draw stress started to fall while above $\sim 6 \times 10^{-2}$ s^{-1} large increases in draw ratio took place. Thermomechanical heating was proposed as a possible reason for these effects.

It is not clear, however, that overall strain rates is the best way of characterising the rate of strain in a neck. Maher, Haward and Hay [48] employed a thermal imaging technique to estimate heating effects during the necking of black polythylene (Density 945 kg m^{-3}). For this purpose a single neck was created and its temperature was recorded at different rates of extension over the range of $0.5–5 \times 10^{-4}$ m s^{-1}. In this way it was found that the temperature at the hottest point in the centre of the propagating neck rose from 10–75% of the value predicted from the work done. Similarly Davis [49], using a test piece of length 15 mm and extension rates of $1.7–17 \times 10^{-3}$ m s^{-1} and the same method of measurement observed temperature rises of up to 40°C. These extension rates corresponded to conventional strain rates of 0.1–1 s^{-1}. However, in Davis's experiment two necks will have been formed. So, for comparison with Maher et al. [48], we get neck extension of rates $8.5–85 \times 10^{-4}$ m s^{-1} as the strain rates over which adiabatic heating develops. While these measurements are not fully comparable it seems safe to conclude that with medium or high density polyethylene adiabatic heating will become highly significant in normal laboratory conditions within the strain rate range of 10^{-2} to 1.0 s^{-1}. At strain rates of 10^2 and above substantial effects are therefore to be expected even with small volumes of material.

6.4. Fibre drawing during fracture

Our estimations of stress–strain relations have shown that adiabatic instability is highly dependent on the level of stress and therefore on the temperature of the material. This means that for high-speed fibre drawing the melt must be raised above a particular temperature. In the fibre drawing processes described by Ishikuza and Koyama [24] a temperature of 210°C is employed which no doubt reflects optimum conditions. They also observed a sharp increase in elongation viscosity around 130°C, the melting point of polyethylene. Our own calculations have suggested that a degree of adiabatic stability might set in above 100°C where fast very large deformation should increasingly become feasible.

In the present work, substantial increases in temperature are predicted during the formation of craze-like structures within the scope of the extension ratios covered by our equations. At the high strain rates characteristic of fast fracture these values might be somewhat exceeded but the results reported by Strobl show that the extensional stresses fall to very low values at 128°C. However in the final stages of fracture this softened material is broken up and torn apart. This occurs with polystyrene where a process of alternating fracture at the two craze matrix interfaces has been identified by Murray and Hull [50] where blocks or blobs of softened material (in the adiabatic case) must be torn apart. Because in fast fracture conditions this material is already hot it is capable of very large fast extensional strains as in high speed spinning. This has been clearly demonstrated with polystyrene where long filaments can be seen on the fracture surface which must represent strains and strain rates much higher than those considered here [31]. If therefore, polyethylene is heated up to temperatures approaching the melting point, it might be expected that such highly drawn fibres would be seen in fast fractures. Although they are not present in the same profusion as have been observed with polystyrene, this appears to be the case. Examples of fibre drawing are observed in most electron micrographs at high magnification as shown in Fig. 15a and b. It is suggested that their presence is evidence of high temperature material in the zone of deformation during the final chaotic stages of fracture.

7. Conclusions

The stable drawing of necked material, as observed in a conventional tensile test with most polyethylenes, is predicted to become unstable under adiabatic conditions. However, the magnitude of adiabatic heating effects is found to depend on the initial temperature of the polymer and to increase when this temperature is reduced. Such temperature rises should reduce the stability of crazes or deformation zones ahead of a crack whenever the fracture process is fast enough for adiabatic conditions to prevail. In a conventional tensile test, under normal laboratory conditions, adiabatic heating first becomes significant when strain rates increase over the range 10^{-2}–1.0 s^{-1}.

It is predicted that temperature rises of 30–80°C should occur during the adiabatic deformation of high crystalline polyethylenes up to extension ratios of 8 or more. Even higher temperatures are momentarily possible when preheated polymer is drawn out during the final stages of fracture.

Mechanical stability should not be greatly affected by minor reductions in crystallinity during a mainly adiabatic deformation process.

Acknowledgements

The authors would like to thank Dr P.S. Leevers for much helpful advice and encouragement. S.H. thanks the E.P.S.R.C. for a grant.

Appendix A

A.1. The volume temperature relation

The linear expansion of polythylenes over a wide range of crystallinities has been determined by Stehling and Mandelkern [21] and these make it possible to derive volume temperature relations over a wide range of temperatures including very low temperatures as shown in Fig. A1. These represent 73% crystallinity material and were corrected by a factor of 0.99 when used for 61% crystalline polyethylene.

A.2. The variation of specific heat with temperature

The values of the specific heat for polyethylene depends strongly on temperature especially at low temperatures. The measurements of Gaur and Wunderlich include values for crystalline and amorphous material over the whole temperature range from zero to the melting point. With these results, together with density measurements, curves may be plotted for heat input per unit volume against temperature for any desired temperature range. The values used for the calculation of adiabatic heating are given in Fig. A2.

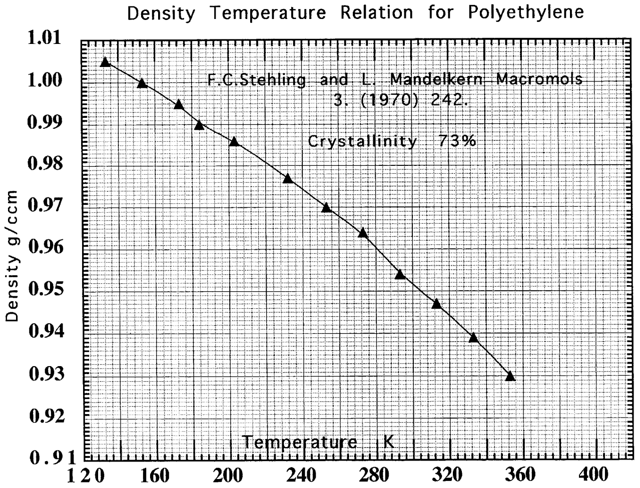

Fig. A1.

A.3. Strain rate and yield stress

There have been a number of measurements of the effect of strain rate on yield stress with polyethylenes, mostly over a more limited range of strain rates than the compression experiments reported by Walley and Field [42]. Two groups of workers have measured the yield stress of polyethylene in tension over a strain rate difference of 10^3 s^{-1}.which can be extrapolated to give a value for 10^4. In this way the results of G'Sell and Jonas [5] gives a ratio of 1.7, while the work of

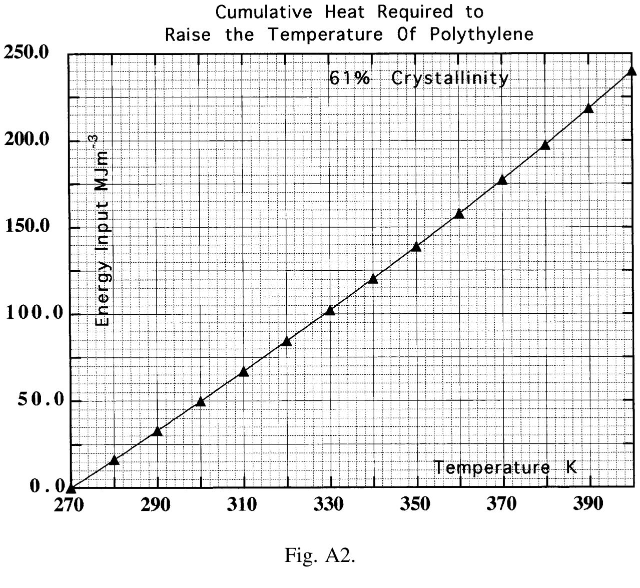

Fig. A2.

Truss, Clarke, Duckett and Ward [51] give values of 1.8 and 2.1 depending on the methods of preparation used for the test piece. This compares with a figure of 1.85 from Ref. [42] over a similar range of strain rates.

A.4. The use of a draw stress

Even with conventional stress–strain curves there can be problems in defining the yield stress although high density polyethylenes nearly always give a well defined maximum at the point where the necking process begins and which would be appropriate in the present case. However this can initiate in different ways but always in a restricted section of the parallel length of the test piece so that the rate of strain at that point is undefined but higher than that generally assumed. Also there seems no reason to extrapolate to zero strain according to Eq. (1). Thus for this purpose it is proposed to use the stress where the true stress–strain curves level out at low strains before strain hardening has become significant. At 24°C this comes to 30 MPa and its associated 65% draw stress 19.5 MPa.

When Fig. 11 is recalculated using this as the constant load the results are qualitatively similar to those given in the figure.

A.5. The conversion of mechanical energy into measurable heat

A recent paper by Pitman [53] has given some operational information about high throughput pelletising extruders used by B.P. Chemicals for polyethylenes. The equipment normally runs under near adiabatic conditions. Asked about the proportion of mechanical work appearing as measurable heat Dr Pitman replied as follows (private communication).

“Regarding the conversion of mechanical energy into heat in the pelletising process, we have indeed performed tests on laboratory equipment where we have tried to minimise the heat flow through the barrel of the extruder and in this case the temperature rise of the polymer reflects closely the energy provided by the drive. Inevitably there is some inaccuracy, possibly arising from the temperature measurement but perhaps also due to the fact that the polymer is not incompressible, so the $P\Delta V$ term is not zero. Consequently the correlation of final temperature with energy via the specific enthalpy data is imprecise. Nevertheless I would say that typically the measured temperature would differ from a theoretically calculated average temperature (estimated assuming all the drive power after correcting for losses through the drive and gear box, is converted into heat) by less than 10°C in a range from ambient to 220°C. This would translate into an uncertainty of less than 5–6% in energy conversion efficiency.

In production pelletising equipment the proportion of heat transferred through the barrel is smaller than in the laboratory experiments. In this case there are some lines, which run on an energy input only slightly higher than the minimum required to melt the material, based on enthalpy data, and yet the material is molten at the die. This means that the conversion of mechanical energy into heat must be relatively high or we would not be able to melt the polymer completely. I would say from plant data that the losses of energy must be no more than 10% — a similar figure to that from the laboratory data”

Although the models of tensile deformation used in this paper are quite different from these extrusion processes it does seem unlikely that the energy conversion ratio will be very greatly reduced so that the β value of 0.5 assumed in some of the calculations presented here should be well below reasonable expectations.

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