The application of a simplified model for the stress–strain curves of polymers

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This paper deals with the application of a semi-empirical equation to true stress–strain curve in the tensile deformation of plastics. In its approximate form the equation is $\sigma_t = Y + K_3(\lambda^2 - 1/\lambda)$ where σ_t is the true stress and λ the extension ratio. Y and K_3 are disposable constants. As true stress–strain curves are not yet freely available for many plastics, the methods of measuring them are reviewed, including three previous reports where the equation was used successfully. The further applicability of the equation is then demonstrated using three further sets of published experimental results. Finally it is shown that the equation may be manipulated to relate the Considère condition for necking and the draw ratio to the constants K_3 and Y.

(Keywords: stress; strain; tensile deformation; stress–strain curves)

INTRODUCTION

The study of large strains in solid polymers continues to attract attention and as new evidence accumulates its importance is increasingly recognized. Indeed, even where brittle fracture occurs, with little average deformation of the test piece, it is known that large localized strains occur at the crack tip, as in a craze[1]. It is therefore desirable to measure large strain behaviour in a systematic way and to provide models illustrating the fundamental factors controlling events.

The most common method of observing large strains is by means of the conventional tensile test, in which one end of a dumbell specimen is extended at a constant rate. However, this test suffers from several disadvantages.

(1) The true length of the specimen may be ill defined. This can be overcome by using bench marks whose movement may be correlated with recorded stress.

(2) The true strain rate, $\mathrm{d}\ln\lambda/\mathrm{d}t$ where λ is the extension ratio and t the time is not constant but decreases as λ increases. Similarly the true stress σ_t (σ_t = applied force/actual cross-section) increases as the cross-section of the material is reduced.

(3) With some materials true strain softening may occur at the beginning of the large deformation process as 'annealed in' or other structures are broken down[2,3]. This leads to a decrease in true stress at low strains and generally promotes strain localization. It does not occur with all materials.

(4) Plastic specimens seldom extend uniformly, instead, deformation is generally localized with the formation of a neck which may then be propagated through the test piece. The resulting stress–strain curves do not correctly reflect the actual response of the material to the applied stress.

The last of these effects represents the most general problem in the study of large tensile strains (e.g. $\lambda > 2$) in plastics. As far as the other effects are concerned, materials which show true strain softening are not covered by the method proposed below. It will also be shown that the quantitative effects due to the systematic change in true strain rate during a test are small (see point (2) above).

TRUE STRESS–STRAIN CURVES

For a systematic study of large strain behaviour it is necessary to measure true stress–strain curves, i.e. σ_t vs. λ for all or part of a test piece. However, as will be clear from the foregoing these are not so easily obtained. However, a number of methods have now been used to provide such curves and these will shortly be listed. Experimental details may be obtained from the references.

(i) *Uniform deformation*

Some plastics will extend uniformly or can be persuaded to do so. A convenient case is that of quenched rigid poly(vinyl chloride), PVC, at low strain rates[4]. A true stress–strain curve in tension for PVC has also been reported by Vincent[5]. Plasticized cellulose esters also show uniform extension although maximum values of λ are generally below 1.5 which limits their value in the study of large deformations.

(ii) *Neck elimination*

With some materials, e.g. low density polythene, considerable further deformation takes place uniformly in material where necking has already occurred. Using bench marks it is then possible to obtain true stress–strain curves at strains above those occurring in the neck[6]. More recently this method has been applied successfully to poly(ether ether ketone) (PEEK)[7].

(iii) *Method of G'Sell and Jonas*[8]

A waisted specimen is extended and the contraction is accurately measured at the narrowest part of the test-piece. No neck is formed and the procedure is computerized to provide a true stress–strain curve in

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tension in the smallest section of the test-piece. This method seems to be more generally applicable than other methods so far reported.

(iv) *Measurements on crazes*

Recently Kramer and Donald[9] have succeeded in measuring the density of polymeric material in a craze and hence the strain in the polymer filaments. Combining these results with estimates of stress enables a true stress–strain curve to be calculated for the material in the craze.

A model for strain hardening

The fundamental model used is the same in principle as that described previously[10] in which a simple Hookean spring is in series with a spring and dash pot in parallel. Here the second spring is assumed to behave like a rubber and the dash pot exhibits an 'Eyring' viscosity.

In this way it follows that strain $= \lambda - 1 = \sigma_E/E +$ plastic strain; where σ_E is the nominal or engineering stress and E the Young's modulus. We may then neglect (or estimate) the Hookean strain (generally less than 0.05 and therefore small for strains > 1) and describe the plastic deformation as follows.

$$\frac{\mathrm{d}(\ln\lambda)}{\mathrm{d}t} = K_1 \exp K_2(\sigma_t - \sigma_R) \qquad (1)$$

where σ_R is a strain hardening term capable of representation by equations related to rubber elasticity[11] and K_1, K_2 are constants according to the Eyring viscosity hypothesis.

At yield the plastic strain is small so that $\frac{\mathrm{d}(\ln\lambda)}{\mathrm{d}t} \sim \frac{\mathrm{d}\lambda}{\mathrm{d}t}$ and as $\lambda \rightarrow 1$ $\sigma_R \rightarrow 0$ so that measurements of the yield stress Y at different strain rates enables K_1 and K_2 to be derived.

We now put

$$\sigma_R = K_3\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (2)$$

as in refs. 4 and 10, and derive a true stress–strain equation viz.:

$$\sigma_t = \frac{1}{K_2}\ln\left(\frac{2}{K_1}\frac{\mathrm{d}(\ln\lambda)}{\mathrm{d}t}\right) + K_3\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (3)$$

Here the first term normally dominates low strain behaviour and the second term is larger at high strains. Furthermore, since the effect of strain rate on yield stress is small for moderate changes in strain rate we will now neglect the effect of changing strain rate during a tensile test, (see also *Figure 2* below) and so obtain an equation previously proposed by Argon[12].

$$\sigma_t = Y + K_3\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (4)$$

and the engineering stress

$$\sigma_E = \frac{Y}{\lambda} + K_3\left(\lambda - \frac{1}{\lambda^2}\right) \qquad (5)$$

Following Vincent[13] we may now consider this equation in relation to the conditions for necking. Applying Considere's condition viz.

$$\lambda \rightarrow 1, \frac{\mathrm{d}\sigma_E}{\mathrm{d}\lambda} < 0$$

where

$$\frac{\mathrm{d}\sigma_E}{\mathrm{d}\lambda} = K_3\left(1 + \frac{2}{\lambda^3}\right) - \frac{Y}{\lambda^2} \qquad (6)$$

we get $Y > 3K_3$ for the condition to be met.

Equation (6) also has a minimum beyond yield as required by Vincent[13] for a material with stable drawing (see below).

Finally, we may propose that at the natural draw ratio λ_D, $\sigma_E = Y$ and so obtain the relation

$$\frac{Y}{K_3} = \frac{\lambda_D - \frac{1}{\lambda_D^2}}{1 - \frac{1}{\lambda_D}} \qquad (7)$$

We will now compare the predictions of the equation with some of the available experimental results. It should also be appreciated that other equations representing the experimental results could also be manipulated to provide similar conclusions.

COMPARISON WITH EXPERIMENT

In work already quoted equation (4) has been shown to represent experimental results satisfactorily for PVC and low density polyethylene and PEEK according to methods (i) and (ii) above[4,6,7].

We shall now apply equation (4) to three further sets of results. The first uses the work of Vincent[5] who reports a true stress–strain relation with PVC. This is plotted in *Figure 1* where a reasonable straight line is obtained. The deviation at the lowest extension is probably due to some true strain softening such as normally occurs with PVC and is rather clearly observed in the work of G'sell and Jonas[8]. These workers apply method (iii) to high density

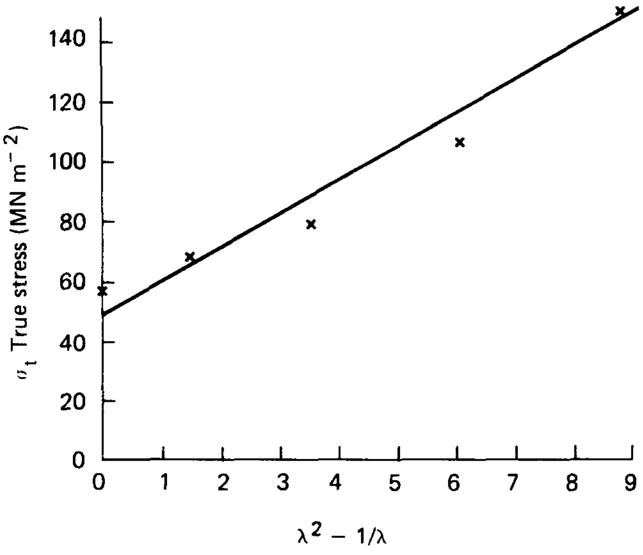

Figure 1 True stress–strain measurements on PVC after Vincent[5] plotted according to equation (4). Intercept $Y = 50\,\mathrm{MN\,m^{-2}}$ Slope $K_3 = 10\,\mathrm{MN}\,,^{-2}$

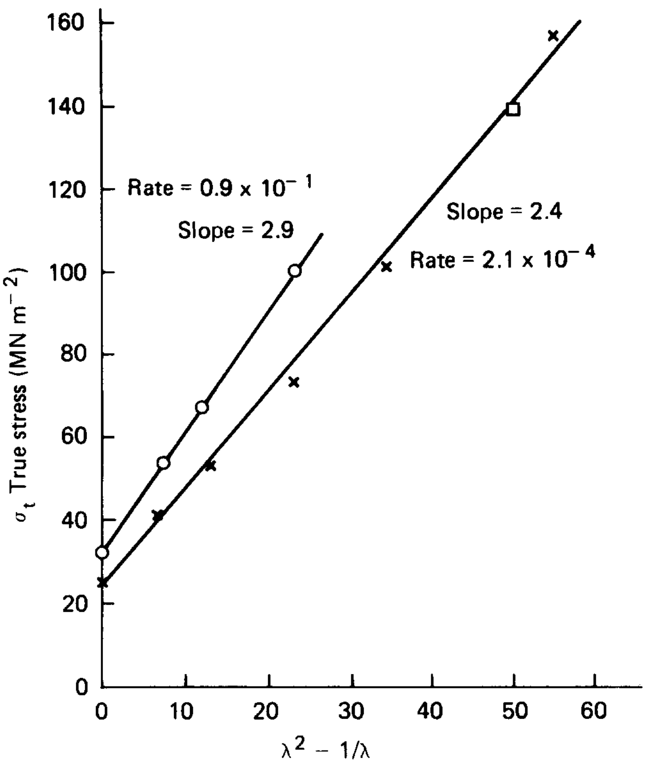

Figure 2 True stress extension ratio plots for HPDE at different strain rates. Intercepts $Y=25$ and 33 MN m^{-2}, respectively (see ref. 8)

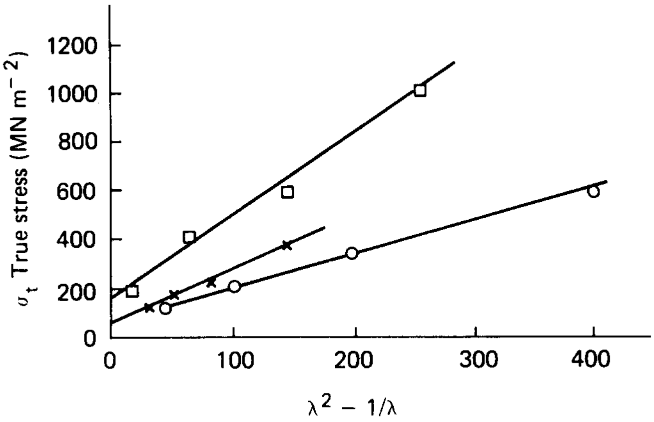

Figure 3 True stress extension ratio plots from measurements on crazes. After Kramer and Donald[8,13]. □, Styrene–acrylonitrile copolymer $Y=160$ $K_3=3.4$, MN m^{-2}; ×, polystyrene. $Y=70$ $K_3=2.2$ MN m^{-2}; ○, poly(t-butyl styrene) $Y=70$ $K_3=1.3$ MN m^{-2}

polyethylene[6], and did not observe any true strain softening, so that their results are suitable for treatment according to equation (4). These are plotted in *Figure 2* where good straight lines are obtained. However, the slopes of the two lines at different strain rates are not the same, as would be implied by a strict interpretation of equation (4). An increase in strain rate by a factor of 500 leads to an increase in slope of 20%. This is not a large rate variation for any polymeric quantity, but does, of course, infringe the principle of K_3 as an equilibrium constant. The Y/K values of 10–11 correspond to a strongly necking polymer. Although no necking occurred in this particular experiment. The squared point on the bottom line (*Figure 2*) shows the small predicted effect of the change in strain rate during extension and supports the suggestion that this factor is not of major quantitative importance in tensile curves.

In *Figure 3* we plot data obtained from a craze by method (iv)[14]. Again a reasonable linearity is achieved as predicted by the equation. However, the values of Y/K_3 are in the region of 30–50 in these cases, owing to the much higher values of Y for the materials concerned.

DISCUSSION

The results generally support previous work[4,6] justifying the application of equation (4). Taken together the results also make it possible to test equation (7) relating draw ratio λ_D to separately measured values of Y/K_3. For this purpose the constants derived from the equation (7) are plotted in *Figure 4* as a continuous curve and values of Y/K_3 from plots of equation (4) are indicated. Predicted values of the draw ratios may then be read off from the curve and compared with known values[15]. Results from these two types of polyethylene point to reasonable draw ratios of 3–4.5 for low density and a rather high value of 9–10, instead of 7–8, for high density grades. Vincent's results for PVC predict a $\lambda_D=3.5$ which is also somewhat high and this is probably because the plotted line has been distorted by true strain softening. The quenched PVC however, which did not neck is close to the Considère limit ($Y/K_3=3$) and although it exceeds it slightly this is probably a real requirement since the Considère condition is simplified and contains no terms to cover the energy required for the distortion of the specimen in the neck.

For interest we also plot the predicted value of λ at the minimum in the engineering stress calculated from equation (6) in *Figure 5*.

A further point concerns the high values of Y/K_3 for the cases of crazing. That these ratios should exceed 3 is certainly expected since a craze may be regarded as an assembly of 'micro necks'. It would also be predicted that high values of Y would be necessary to supply energy for cavitation and the formation of fresh surfaces[15,17]. The possibility that high values of Y and Y/K_3 are correlated with crazing behaviour is also an attractive possibility but lacks adequate evidence.

Finally, it seems necessary to make some comments on

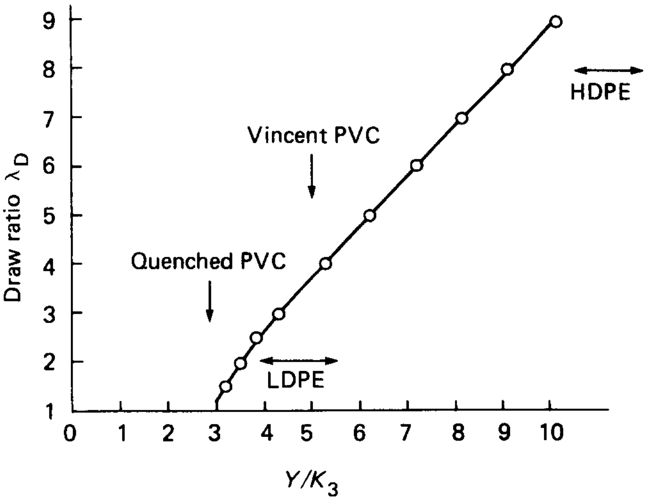

Figure 4 Predicted draw ratio against Y/K_3 according to equation (7). Experimental values of Y/K_3 obtained from previous curves

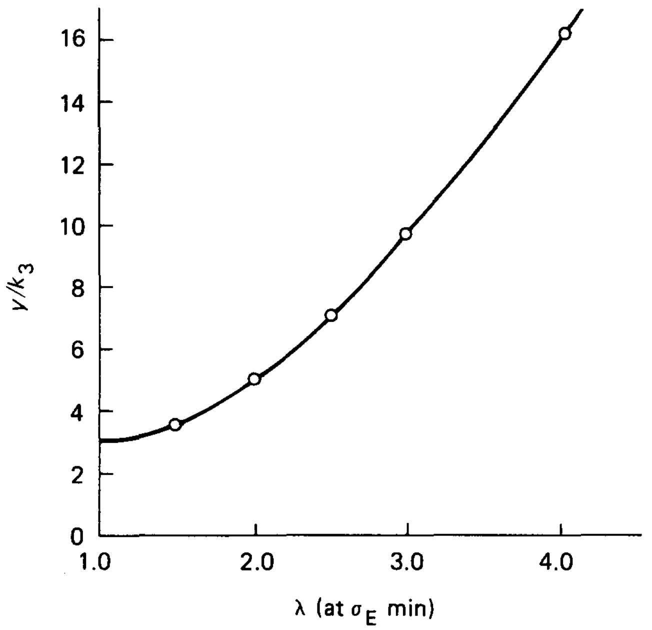

Figure 5 Values of λ at the minimum in the engineering stress plotted according to equation (6)

the nature of K_3. Initially K_3 represented the known equilibrium behaviour of rubbers[11] but it has been used here essentially as an empirical constant defining strain-hardening behaviour. It could be that there is a mathematical analogy between rubber elasticity and a strain-hardening process controlled by the exhaustion of deformable bends. In order to find out more about the nature of the process it would be necessary to evaluate equation (4) for a wider range of materials and conditions. The present level of knowledge simply reflects the paucity of true stress–strain curves for plastics. This especially applies to the effects of temperature. For example, if K_3 were a true rubber elasticity constant related to a geometrical level of entanglements then it would increase with temperature. There are, however, indications that this is not the case. For example, Marshall and Thompson[18] showed that the draw ratios of poly(ethylene terephthalate) did not change between 20°C and 40°C although the yield stress did change. Furthermore, Kastelic and Baer[19] found that the fall in engineering stress of polycarbonate after yield decreased as the temperature was lowered from 350 to 100 K. Both results appear incompatible with an increase in K_3 with temperature within the framework of equation (4). This, of course, reflects on the interpretation rather than the applicability of the present proposals.

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