The derivation of a strain hardening modulus from true stress–strain curves for thermoplastics*

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Some problems in the measurement of stress–strain curves for thermoplastics are considered and the importance of measuring true stress–strain curves is emphasized. However, an increasing number of suitable curves have now been published of which the large majority have been found to comply with the following Gaussian equation:

$$\sigma_{\text{true}} = Y + G_{\text{P}}(\lambda^2 - 1/\lambda)$$

where σ_{true} is the true stress, Y is the extrapolated yield stress, G_{P} is the strain hardening modulus and λ is the extension ratio. It is shown that the Considere condition for necking requires that $Y/G_{\text{P}} > 3$ and the available results support the proposition that this is a necessary condition for necking to occur. High values of G_{P} are observed in polymers with an extended chain conformation.

(Keywords: strain hardening modulus; stress–strain curves; thermoplastics)

INTRODUCTION

When a thermoplastic test piece is subjected to a uniform rate of extension the applied stress increases steadily until either yielding or fracture take place. Both processes have been studied extensively and, in particular, numerous measurements have been made on the process of yielding and a number of mechanisms proposed[1,2]. Once yielding has been initiated it can continue until very large deformations are produced. Such post yield deformations have been the subject of numerous experimental studies but so far no quantitative theory or generally accepted interpretation has emerged. However, some time ago it was proposed that the post yield deformation could be represented by a model comprising a spring and a dashpot in parallel[3,4]. The particular feature of this model was that the spring should comply with the laws of rubber elasticity[5].

In the first application of this proposal, the Langevin equation was used to represent the elastic component, and the equations were computed and compared with conventional stress–strain curves[4]. The results generally followed the form of typical stress–strain curves but good quantitative agreement was not achieved. Furthermore, the use of the Langevin relation complicated the application of the model and necessitated difficult computer calculations. Partly for this reason little progress was made over the next 10 years although Argon[6] pointed out that if the Gaussian elasticity relation was substituted for the Langevin theory a true stress–strain curve could be simply represented by the following equation:

$$\sigma_{\text{true}} = Y + \text{constant } (\lambda^2 - 1/\lambda) \tag{1}$$

where σ_{true} is the true stress, i.e. a stress which is uniform over the volume of material under consideration, Y is the yield stress, and λ is the extension ratio (λ = extended length l/original length l_0). This equation will be subsequently referred to as the Gaussian equation. In principle its evaluation against experimental results should be a straightforward matter, but this has been hindered by experimental difficulties which will be described in the next section. Although many conventional stress–strain curves had been recorded in the literature, very few of these could be used to provide suitable true stress–strain curves at the time these proposals were first reported.

THE PROBLEMS OF MEASUREMENT

The experimental difficulties in measuring true stress–strain curves may be illustrated by considering the course of events in a conventional tensile test. In this test a dumb-bell shaped test piece is gripped between the two jaws of a tensile testing machine, one of which moves outwards at a constant rate. Simultaneously, the machine measures the force applied to the test piece and records the results in the form of a load–extension curve. This may be converted to an engineering or nominal stress–strain curve using the parallel length of the test piece and the initial cross-sectional area. This procedure involves one major limitation and two relatively minor inaccuracies.

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Of the minor problems the first relates to the form of the test piece. Normally the stress rises in the later stages of a test, and when this occurs the deformation is not confined to the parallel length of the test piece and spreads into the shoulders of the dumb-bell. Under these conditions the appropriate length of the test piece is not properly defined. This difficulty is eliminated when bench marks are used to measure the extension of the material, The second difficulty concerns the variation in the strain rate which is known to affect the value of the yield stress Y. The true strain rate should be defined as $\mathrm{d}\ln\lambda/\mathrm{d}t$ and this falls steadily when the test piece is extended at a constant rate[4,7].

The major problem arises from the manner in which the large deformation process actually takes place in a tensile test. Only exceptionally does a thermoplastic deform in a uniform way as with the cellulose esters used in reference 4. More commonly the deformation process is localized to give crazes, necks or shear bands. With some materials such as impact polystyrene deformation may appear to be uniform but actually consists of a large number of crazes with associated microvoids[8]. When any of these effects are present the measurements calculated from the instrumental record fail to describe the deformation process in any part of the test piece.

There are two ways of dealing with this problem. (1) Where possible, a test piece which will deform uniformly should be selected or prepared. This has been done by Haward *et al.*[4,9,10], by Biddlestone *et al.*[11] and by Levita and Struik[12]. Generally the differences between true and nominal strain rates were neglected in this work, and this will be discussed later. (2) More generally, the deformation process may be observed in a selected part of the test piece where deformation is effectively homogeneous. This method has been employed by G'Sell *et al.*[7,13,14] and by Hope *et al.*[15]. Both studies employ a sharply waisted test piece and G'Sell *et al.*, in particular, have developed a sophisticated procedure in which the strain is measured at the narrowest part of the waist by passing a taut wire round the circumference. A constant strain rate, measured as $\mathrm{d}\ln\lambda/\mathrm{d}t$, is then maintained by controlling the rate of extension through a computer. These workers have applied their technique to a wide selection of different thermoplastics and published a number of true stress–strain curves.

Examples will now be given of the results obtained when measurements made with the two different experimental methods are plotted according to equation (1). Since the publication of the first Gaussian plot[15], there have been several papers published in which a number of different thermoplastics have been shown to comply with the Gaussian equation[12,16,17] The results now available include 15 different thermoplastics with 20–30 separate plots, so that one may conclude that the majority of thermoplastics give true stress–strain curves in tension which follow equation (1).

In plotting actual experimental curves in accordance with the requirements of equation (1), however, some problems arise with the first part of the stress–strain curve. In the original paper[4], a Hookean spring was placed in series with the parallel spring and dashpot. By combining this with an Eyring viscosity to represent the effect of strain rate on the yield strength Y, it was possible to compute a presentable stress–strain curve right from the point where the stress was first applied, i.e. including the part where mixed Hookean and plastic deformation take place. However, since that work was reported it has become clear that there are a number of special 'beginning' effects during the first stage of the plastic deformation process. These may include initial stress peaks which are strongly dependent on the previous thermal history of the material (annealing peaks) [18,19] and plastic shear transitions which store energy at the initiation of plastic strain and are believed to reflect local distortions of structure[20]. Changes in the proportions of different rotational isomers also occur during deformation[21] and these changes may be especially large in the early stages of plastic deformation[22]. Thus a number of plastics exhibit beginning effects which are absent in the later stages of the deformation process. These problems may be largely avoided by starting the Gaussian plot at λ values of 1.1–1.3, in which case the Hookean extension may generally be neglected. Where this is not appropriate, a Hookean strain may be estimated and subtracted from measured values of λ. Examples of Gaussian plots derived from the two methods of measurement will now be given.

SURVEY OF SOME TYPICAL DATA

Uniform deformation

Rigid poly(vinyl chloride) (PVC). In a normal tensile test PVC sheet will show an initial stress peak followed by necking[19]. However if the sheet is heated above its glass transition temperature (T_g), and then quenched in ice-water the size of the peak is greatly reduced and a suitable test piece can give uniform deformation at low rates of extension. The first Gaussian plot was obtained in this way (*Figure 1*)[9]. Uniform deformation can also be obtained when the PVC is softened with a small amount of plasticizer. The quenched material also gave an equivalent Gaussian plot in plane strain compression, although in this case the appropriate equation is:

$$\sigma_{\mathrm{true}} = Y + \mathrm{constant}\ (\lambda^2 - 1/\lambda^2) \qquad (2)$$

Cellulose acetate butyrate (CAB). Although the cellulose esters give uniform deformation under tension they tend to fail at rather low strains, e.g. $\lambda < 1.5$. Since the plastic deformation process cannot easily be measured at low values of λ this leaves only a short range of extensions available for plotting and may be inadequate for establishing the validity of equation (1). However, Levita and Struik[12] have published a curve for CAB which extends to λ values of 1.9 and which gives a good Gaussian plot as shown in *Figure 2.*

Poly(aryl ether ether ketone) (PEEK). This material necks under tension but after passing through the neck it is capable of a significant further homogeneous extension which, with the aid of bench marks, can be used to provide a true stress–strain curve. The results published by Biddlestone *et al.*[11] are shown in *Figure 3.* Results are plotted for semicrystalline and amorphous materials and give good straight lines though with different intercepts and slopes. This suggests that the underlying mechanism of the stain hardening process is similar for both semicrystalline and amorphous polymers.

Uniform deformation measured in a restricted volume of the test piece

As already indicated, G'Sell and Jonas have devised a method for measuring a true stress–strain curve using a

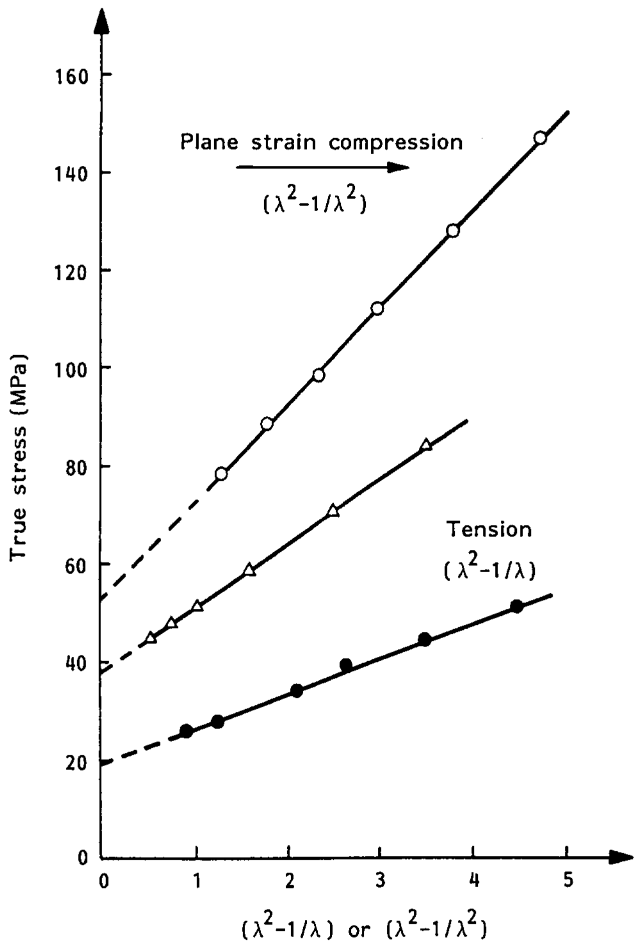

Figure 1 True stress–strain plots for rigid quenched poly(vinyl chloride) (PVC) in tension (△) and plane strain compression (○), and lightly plasticized PVC in tension (●)

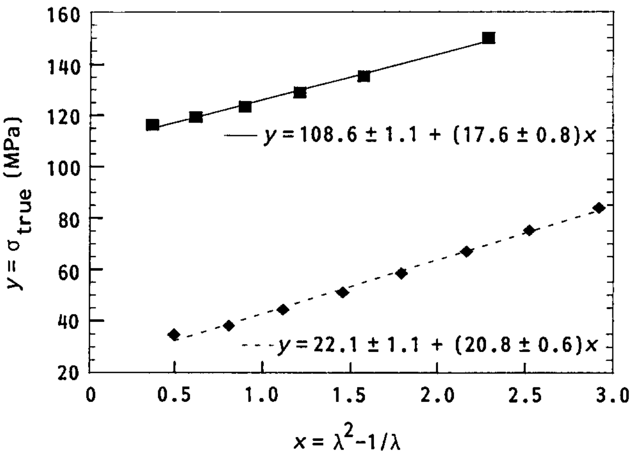

Figure 2 Gaussian plots for cellulose acetate butyrate (◆)[12] and poly(aryl ether ether ketone) (■)[13]. The reference numbers relate to the source of the original data

cylindrical waisted test piece. With this technique they have reported results with a wide range of thermoplastics which, with the exception of polycarbonate, follow the Gaussian equation. Their results for high density polythene (HDPE)[7] were reported at a number of different strain rates, two of which are plotted in *Figure 4*. The good linearity observed was confirmed in later work on a series of polymers at a single strain rate. It will be seen that the effect of strain rate on G_P is less than that on Y. This is generally in accordance with the model, since Y represents a viscosity or yield strength for which a dependence on strain rate would be expected. The variation in G_P on the other hand, although smaller than for Y would not be predicted by rubber elasticity theory which is based on equilibrium. By using the two curves and assuming a linear relation between log strain rate and stress[4,7] it is possible to estimate the line that would have been obtained in an experiment in which a constant rate of extension was applied under conditions of uniform deformation. This is represented by the dotted line in *Figure 4*. It will be seen that the linearity of the calculated points is not affected by the variable strain rate, though G_P is reduced by ~10%. This supports the general validity of conclusions from experiments with uniform deformation as does the similarity of results for low density polyethylene from G'Sell and Jonas[13] and from Mills *et al.*[10] (see reference 16).

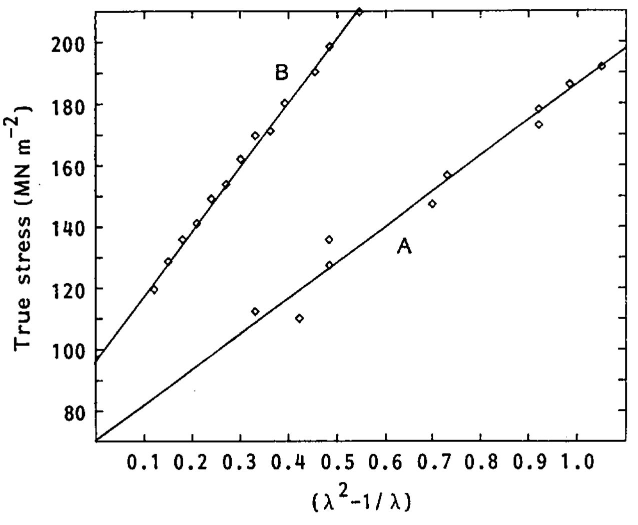

Figure 3 Gaussian plots for (A) amorphous and (B) semicrystalline materials. Both plots follow equation (1). Crystallization does not affect the linearity of the Gaussian plot

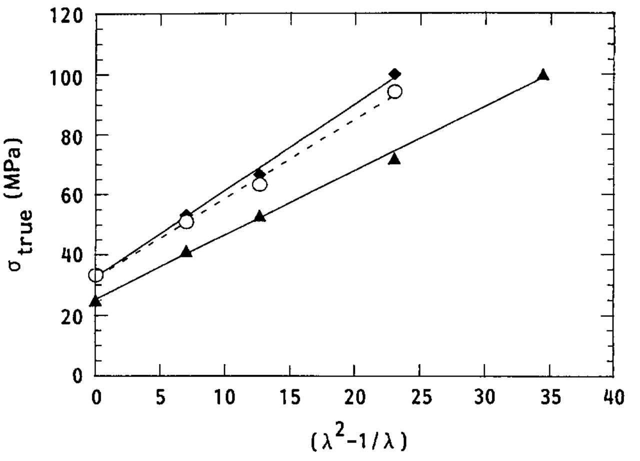

Figure 4 Gaussian plots for high density polyethene. The solid points are from the work of G'Sell and Jonas[7] and their lines give $Y = 33$, $G_P = 2.9$ and $Y = 25$ and $G_P = 2.4$, respectively. The dotted line is calculated for a test piece whose strain rate decreases with λ as if the sample deformed in a uniform way with a constant rate of extension (○). Strain rate: (▲) 2.1×10^{-4}; (◆) 0.9×10^{-2}

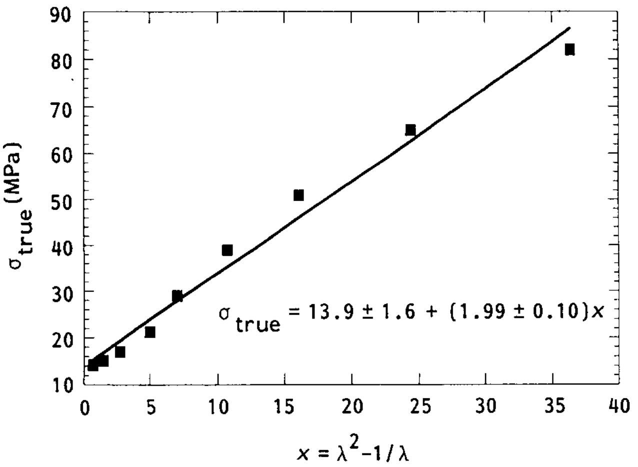

Figure 5 Gaussian plot for low molecular weight poly(methyl methacrylate) at 90°C. The fit to the Gaussian equation is not as good as with other results at lower temperatures, though the errors in the predicted stress are within $\pm 15\%$. Points taken from reference 15

PEEK. Measurements by G'Sell *et al.* have already been included in *Figure 2*[14,15]. They may be compared with those obtained by the uniform deformation post yield procedure by Biddlestone *et al.*[11] shown in *Figure 3*. Both sets of results agree in finding that PEEK is a polymer with a high value of the extrapolated yield strength and a high value of G_P but the results of reference 11 with the crystalline material differ from those of G'Sell *et al.* by a factor of $\sim 10\%$, a difference which seems as likely to derive from actual differences in the two materials as from differences in the experimental method.

Application at higher temperatures

The original model was conceived as having its application at temperatures well below T_g or the melting temperature (T_m), so that equilibrium between different chain conformations did not take place, though the availability of highly extended conformations would diminish as λ increases in accordance with the theory of rubber elasticity[5]. Thus it was anticipated that the models might fail as the temperature was increased. However, the measurements of Hope *et al.*[15] for low molecular weight poly(methyl methacrylate), using a waisted specimen, give a reasonable fit to the Gaussian model (*Figure 5*) but similar measurements with a higher molecular weight polymer gave an increased level of hardening at high strains and did not fit the Gaussian model. These have been shown by Boyce *et al.*[23] to comply with the Langevin equation. A similar departure from the Gaussian model has been found for polystyrene at 96.4°C[14,16] and for HDPE at 90°C[16,24]. It has also been found *at normal temperatures* that ultra high molecular weight polyethylene gives higher levels of strain hardening than predicted by the Gaussian equation at high strains. Thus, the effect of a high molecular weight is consistent with the idea of a more permanent system of entanglements with this type of material. The effect of temperature is not so suggestive but may indicate a certain permanence of entanglements when the polymer is deformed at low stresses. However, for the time being such conclusions must remain rather speculative in the absence of more systematic experimental results.

CONSIDERE CONDITION FOR NECKING

The use of the Gaussian equation to represent the large deformation process has a number of advantages. Foremost among these is its relative simplicity which makes it easy to calculate the amount of strain hardening at a particular strain. It is also possible to substitute for Y any of the suitable relations which describe the variation of yield stress with strain rate[1,2]. The same argument applies in principle to the effect of temperature, but this is complicated by large variations in G_P which are not properly understood (see below). Equation (1) may also be rearranged to represent the nominal or engineering stress σ_{eng} as shown below:

$$\sigma_{eng} = Y/\lambda + G_P(\lambda - 1/\lambda^2) \qquad (3)$$

Using this form of the equation it may be noted that Considere's condition for necking requires that at low values of λ, $d\sigma_{eng}/d\lambda$ is negative i.e.

$$d\sigma_{eng}/d\lambda = -Y/\lambda^2 + G_P(1 + 2/\lambda)^2 \qquad (4)$$

should be <0 when $\lambda = 1$, for which the critical condition is $Y/G_P > 3$. It is important to appreciate here that λ applies only to the plastic deformation and that the Hookean contribution is not included.

Consideration of the examples given here shows that CAB with a ratio of 1.1 does not neck and neither does PVC with a ratio of 2.9. However, the PVC shows marginal behaviour and the deformation would start to become inhomogeneous if the strain rate was increased (with consequent increases in Y). More usually PVC exhibits marked annealing peaks which raise the yield strength and cause necking in conventional tensile tests. Apart from CAB, values of $Y/G_P < 3$ have been recorded for three other materials[16] (cellulose nitrate, polyisocyanate and polyimide DPO), all of which show uniform extension. Although more examples would be desirable, there are no known exceptions to the rule that polymers with $Y/G_P < 3$ do not neck under conditions of isothermal extension. On the other hand, in the range of Y/G_P of 3–4.5 there is some variability as shown by PVC. For example, ultra high molecular weight polyethylene has a value of ~ 4.4 and does not neck at low strain rates[16]. So, while more measurements would again be an advantage, it seems that values somewhat above 3 may be required for reproducible necking. Obviously no detailed account of the necking process can be given purely in terms of tensile deformations so that in the marginal region around three, other factors may determine behaviour. In accordance with expectation, the polymers which characteristically neck under a wide range of conditions have high ratios, e.g. HDPE, polypropylene, polyamide 6, polyamide 66 and PEEK all have values of $Y/G_P > 4.5$.

RELATION BETWEEN STRAIN HARDENING AND MOLECULAR STRUCTURE

At present there is no general understanding of the relation between strain hardening and molecular structure. Indeed the problem may be regarded as forming part of a more fundamental relationship between deformation and entropy in a mesh of polymer molecules without crosslinks. However, this subject is now attracting some attention. It has been considered by Graessley and Edwards[25] and applied to the case of the plateau modulus which can be measured on thermoplastics at temperatures above T_g or T_m. They proposed that the modulus should increase with higher values of the Kuhn length. According to this proposal, polymer chains with more highly extended conformations would have a greater degree of interpenetration (entanglement) and therefore a greater restriction of conformational changes. This proposal has been suppored by Prevorcek and de Bona[26] who worked with polyarylates and by the work of Bosnyak *et al.*[27] who studied the effect of molecular structure on strain hardening with similar polyarylates. It is also in agreement with the present measurements of G_P. For example, the cellulose esters and the polyisocyanates which have high values of G_P and low values of the ratio Y/G_P also have high values of the Kuhn length. More detailed conclusions are hard to justify at the present stage as G_P and Y both vary with temperature and this complicates comparisons between different polymers. Only when the differences are relatively large is it possible to reach definite conclusions.

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