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Strain Hardening of Thermoplastics

R. N. Haward

Department of Chemistry, University of Manchester and UMIST,
Manchester M60 1QD, England

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ABSTRACT: Most of the published stress–strain curves for thermoplastics are of limited theoretical interest as the test piece does not deform uniformly. However, over the last 20 years, several methods have been developed which enable true stress–strain curves to be obtained. This can be done either by using a polymer which is capable of uniform deformation or by confining the measurement to a small volume of the test piece in which uniform deformation may be assumed. The results so obtained can be interpreted by means of a spring and dashpot model in which the spring defines a strain hardening process according to the theories of high elasticity. When conventional Gaussian chain statistics are employed to represent the spring, the plastic deformation is represented by the equation $\sigma_{\rm True} = Y + G_{\rm p}(\lambda^2 - 1/\lambda)$ where $\sigma_{\rm true}$ is the true stress, Y the extrapolated yield stress, $G_{\rm p}$ a strain hardening modulus, and λ the extension ratio λ = extended length (l)/original length $(l_{\rm o})$ Most crystalline polymers obey this relation at temperatures significantly below their melting point $(T_{\rm m})$. In some cases, this agreement extends to very high values of λ, as with high-density polyethylene where the equation has been followed up to λ values of 12. With glassy polymers, difficulties may arise when a true strain softening effect occurs at the beginning of the extension process. Sometimes, as with PVC, this effect disappears at low strains and eq 1 is obeyed above $\lambda \sim 1.2$, but with polycarbonate the strain softening extends to high values of λ and appears to distort the whole stress–strain relation. It is proposed that the modulus $G_{\rm p}$ is determined by the sum of the restraints imposed by a mesh of uncrossable polymer chains. Attempts to interpret $G_{\rm p}$ in terms of a conventional entanglement molecular weight give generally unacceptable results except in the case of polyethylene. Polymers with an extended chain conformation (high values of the Kuhn length) have high values of $G_{\rm p}$. A ratio of $Y/G_{\rm p} = 3$ corresponds to the Considere condition for necking and gives a good indication of plastic instability.

1. Introduction

During the last 20 years, several methods have been devised to measure the true stress–strain curves of different thermoplastics in tension. In this paper, published curves are used to evaluate a theoretical equation derived from a model in which the strain hardening effect is related to the Gaussian network theory of rubber elasticity. The results are compared with previous work and listed in tables and appendices.

In assessing the significance of the treatment, it is first necessary to consider the problems of measurement. Numerous measurements of stress–strain curves of thermoplastics have been reported in the literature over a long period, but, unfortunately, many of them are unsuitable for quantitative evaluation. There are many reasons for this situation. Most commonly such curves are obtained by stretching a dumbbell-shaped test piece in a tensometer and relating stresses to the original cross section, i.e., to the nominal or engineering stress $\sigma_{\rm Eng}$. The corresponding strains are then measured in terms of the parallel length of the test piece. Here the use of parallel length incurs minor errors, which are eliminated when benchmarks are employed. More serious problems arise from the response of the test piece itself. Only exceptionally, as with the cellulose esters, does the deformation take place in a uniform manner, usually the test piece develops necks, shear bands, crazes, or voids, i.e., the strains vary in different parts of the test piece. In such cases the data obtained using the machine cannot be employed in a theoretical study of stress–strain behavior. Only in cases where the polymer responds by uniform deformation or where the volume of material studied is sufficiently small for this to be assumed is it possible to convert $\sigma_{\rm Eng}$ into $\sigma_{\rm True}$ and to compare the results with theoretical models.

However, over a rather long period an increasing number of the true stress–strain curves have been reported from a number of sources. Some of these have been obtained by a special technique developed by G'Sell and Jonas which uses a waisted specimen to avoid necking.[1–4] In other work it has been possible to select polymers which are wholly or partially able to extend in a uniform manner.[5,6] Some true stress–strain curves have also been estimated in the course of a detailed study of crazing.[7]

However, in a few cases the problems associated with measuring true stress–strain curves have not been overcome. This situation arises with certain types of inhomogeneous deformation where cavities are formed within the polymer. For example, with high-impact polystyrene large numbers of crazes are formed[8] and with poly(1-butene) a more dispersed system of voids is generated.[9] In neither case has a representative true stress–strain curve been obtained.

Another type of behavior where the measurements cannot be interpreted in terms of the theory proposed in this paper is where true strain softening[10] (or intrinsic yield drop[11]) is observed. This occurs at the beginning of the deformation process and includes a number of complicating factors[12–14] which will be discussed later, together with the well-known effect of physical aging or annealing in raising yield stress. The latter is believed to be removed once yielding gets under way.[15,16] Both polycarbonate[2,4] at normal temperatures and high molecular weight poly(methyl methacrylate) at elevated temperatures (ref 4 and Figure 16A of ref 17) show large initial falls in true stress which preclude treatment according to the theory proposed here.

2. Theory of Stress–Strain Curves

The theory proposed by Haward and Thackray[18] is illustrated in Figure 1. Figure 1a shows a Hookean spring

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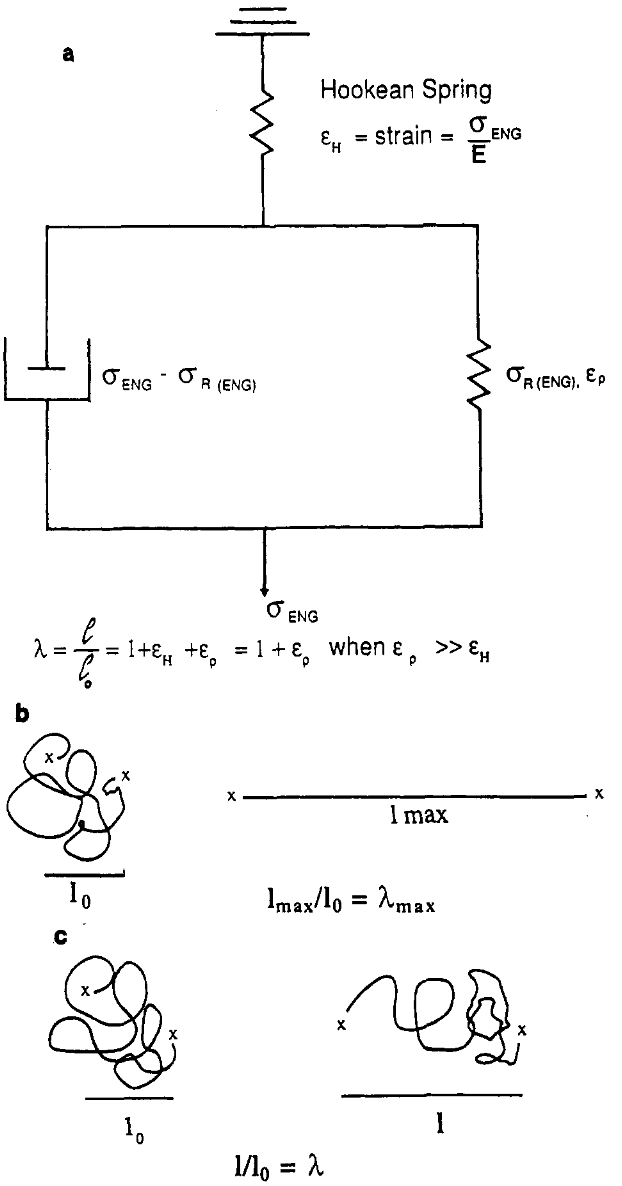

Figure 1. (a) Model for large strains in thermoplastics. The model may be used equally for engineering or true stresses. (b) Langevin equation applies when the polymer chain approaches its maximum extension between entanglements. (c) Gaussian equation describes the distortion of a statistical coil.

in series with a dashpot in parallel with another spring. This is assumed to generate a stress ($\sigma_{R(Eng)}$ or $\sigma_{R(True)}$) in accordance with the theories of rubber elasticity.[19] In applying the model, the following quantities are used

$$\text{extension ratio } \lambda = \frac{\text{extended length}}{\text{original length}} = \frac{l}{l_0} = 1 + \epsilon_H + \epsilon_p$$

where ϵ_H and ϵ_p are the Hookean and plastic strains respectively

$$\sim 1 + \epsilon_p \quad \text{when } \epsilon_p \gg \epsilon_H$$

Thus ϵ_H may either be neglected or estimated from the initial part of the curve and subtracted from subsequent measurements.

The model may be applied in two ways.

2.1. Using the Langevin Equations (Figure 1b). The first application of the above model used the Langevin equation for rubber elasticity at high strains.[19] This assumes that the polymer chain is extended between permanent points of entanglement until it is nearly straight and so provides a limiting ultimate elongation λ_{max}.[7,18] In applying this procedure, two constants are required to describe the strain hardening effect: (a) the Kuhn length *A* which may be derived from the molecular coil configuration in the solid state or from a solution in a Θ solvent.[7,18,20] (b) The number "*n*" of Kuhn lengths between points of entanglement. Instead of *n* other quantities such as entanglement density or mesh size may be used, leading to slightly different mathematical expressions.[19] In all cases, the Langevin equation requires an upper limit to the value of λ, i.e., $\lambda_{max} = n^{1/2}$.[18-20]

2.2. Using the Gaussian Equation (Figure 1c). In the Gaussian treatment the polymer coil does not approach a fully stretched condition and the elastic stress can be represented by

$$\sigma_{R(True)} = \lambda\sigma_{R(Eng)} = G_p(\lambda^2 - 1/\lambda)$$

where G_p may be called the *strain hardening modulus.* Then at constant strain rate

$$\sigma_{True} - \sigma_{R(True)} = Y = \text{constant}$$

so that

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

Equation 1 formalizes the assumptions of the Gaussian alternative model for large plastic strains as described above. In the following work it will be more shortly referred to as the "Gaussian model" or the "Gaussian equation". Its application to the case of uniaxial tension is the main subject of this paper. In principle, however, the model may be applied to other types of plastic strain, e.g., to plane strain compression[5,6] when the equation becomes

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

Equation 1 is readily transposed to engineering stresses to give

$$\sigma_{Eng} = Y/\lambda + G_p(\lambda - 1/\lambda^2) \tag{3}$$

As previously stated,[21] this equation has a maximum value at low strains when $Y/G_p > 3$ which coincides with the Considere condition for necking.[21,22] Thus at high ratios of Y/G_p there will be a minimum in σ_{Eng} at higher values of λ, after which it will increase again, thus meeting Vincent's condition for stable necking.[22]

Using the above model, Argon[23] first proposed eq 1 and later it was separately derived from the Rivlin–Mooney theories by Cross and Haward and shown to agree with experimental results on PVC.[5] It has since been evaluated in several further studies.[3,6,21] In this paper the equation will be evaluated against published results not previously used for this purpose though, in one or two cases, graphs will be shown which extend the range of data previously treated.[3] It is hoped to demonstrate the very wide range of thermoplastics which comply with the Gaussian model and to clarify the factors which cause the minority of materials to behave differently. A summary of data from published Gaussian plots is given in Appendix I, and Appendix II shows a list of polymers whose stress–strain curves have been found to depart from the Gaussian model.

3. Application of the Gaussian Equation to Published Stress–Strain Curves

The graphs presented in this paper are based on published true stress–strain curves and on engineering

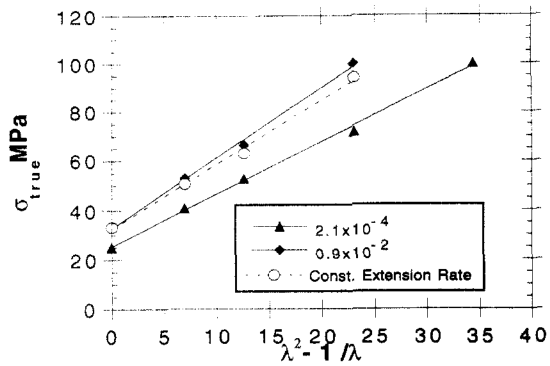

Figure 2. Effect of changing strain rate during uniform deformation and constant extension rate. Estimated from the results given in refs 1 and 21 for high-density polyethylene (HDFE).

curves where the polymer extended uniformly. Published curves from several different sources were enlarged and extra grid lines drawn over them. Representative points could then be measured off for computer plotting.

It is not proposed to detail here the experimental aspects of measuring true stress-strain curves which have been discussed elsewhere.[1,4,18,21] Ideally, true stress-strain curves should be measured at a constant true strain rate d ln λ/dt, but curves at constant rates of extension are also treated here and it is therefore appropriate to indicate the errors involved when this method is employed.

3.1. Errors in a Constant Rate of Extension Experiment. The limitations of this type of test apply to all the results used in this paper except those published by G'Sell and co-workers.[1-4] An estimate will therefore be made of the nature and magnitude of the errors introduced by the change in strain rate when a uniformly extending material is subject to extension at a constant crosshead speed and therefore at a steadily diminishing true rate of strain. This may be done when true stress-strain curves are available at different strain rates, as with high-density polyethylene (HDPE).[21] As these results give good Gaussian plots, it is possible to adjust the points for the line at the higher strain rate for the condition of a constant speed of extension assuming proportionality between stress and log strain rate.[3,18,24] The resulting points give the broken line in Figure 2. It will be seen that the linearity of the Gaussian plot is not affected by the changes in strain rate but that the slope is reduced by about 10% (2.88 → 2.64). As HDPE gives a relatively large change in stress at different strain rates compared with other polymers,[3] the correction is probably larger than would normally be the case.

3.2. Results from the Method of G'Sell and Jonas. The results of G'Sell and co-workers[14] are particularly suited to the quantitative evaluation of stress-strain curves. Examples of their published curves, reproduced from ref 2 are given in Figure 3. With the exception of polycarbonate, which shows a pronounced true strain softening effect, all the curves give good agreement with the Gaussian method as already demonstrated by G'Sell and Jonas.[3] Three of what are apparently the same curves taken from ref 2 have also been plotted according to the Gaussian equation by the present author using the method described.[25] Values for the constants Y and G_p measured by the two methods are given in Appendix I (parts B and C of Table I). Differences between the two sets of results arise from errors in reproduction, the application of computer lines, and greater weighting of high λ values in the present work. In his latest work G'Sell et al.[4] improved their experimental method to include the use of higher temperatures. In this way they made measurements on polystyrene and poly(oxymethylene) which are plotted according to eq 1 in Figure 4, although the polystyrene is probably too near its glass transition temperature to give a good straight line. Other results from ref 4 are given in the sections appropriate to the materials.

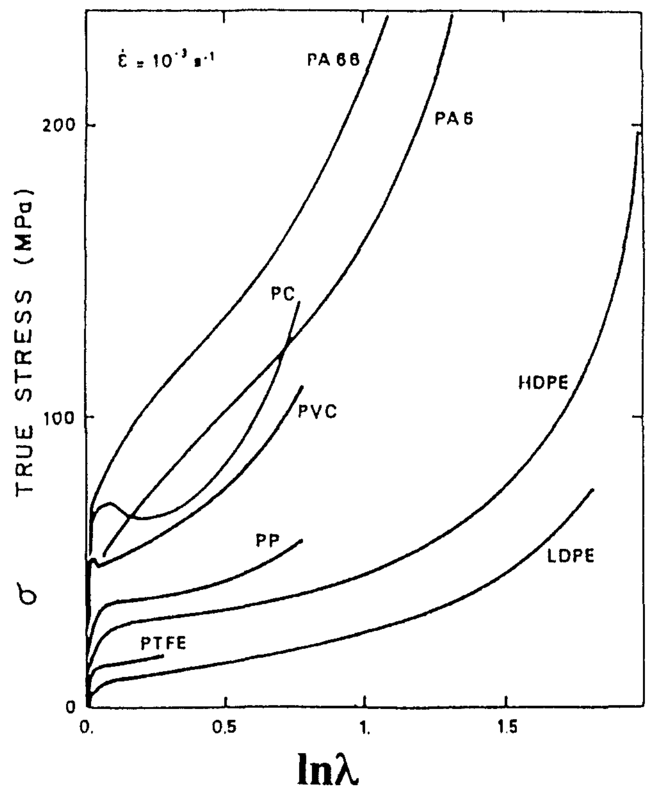

Figure 3. Typical example of true stress-strain curves from G'Sell.[2] Reproduced by permission of "Les Editions de Physique", 91944 Les Ulis, France. Except for polycarbonate (PC) these curves all comply with the Gaussian model. This was shown by the author in another paper,[3] and similar results were obtained by the methods described in this paper.[25] The measurements of G'sSell and Jonas provide for a constant true strain rate d ln λ/dt, and they make their results consistent by reporting all strains in terms of ln λ which they then specify as true strain. In this paper true strains are defined as those which properly represent the behavior of the material under test. They may be measured as λ, ln λ, or even by percent extension.

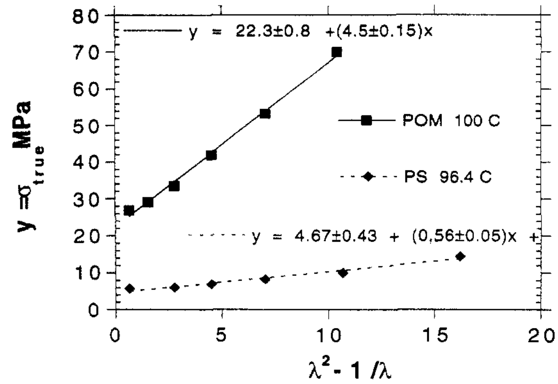

Figure 4. Gaussian plots for poly(oxymethylene) and polystyrene at elevated temperatures.[4] Poly(oxymethylene) gives a satisfactory Gaussian plot, but the polystyrene shows an upward (concave) curvature which would be more obvious on an expanded Y scale (see Appendix II).

3.3. Polyimide DPO. The author is indebted to Drs. Bessonov and Laius for a series of stress-strain curves measured on the polyimide DPO.[26] Over a wide range of temperatures, this polymer gives a series of curves showing uniform extension and does not craze or neck.[10,26-28] It is

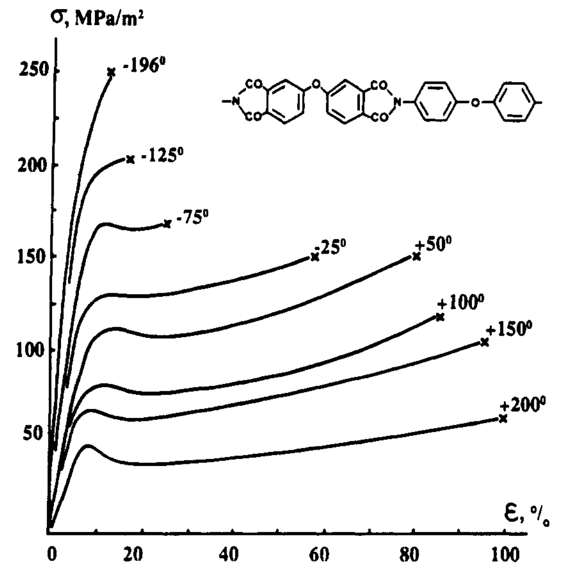

Figure 5. Engineering stress–strain curves for polyimide DPO* at different temperatures. Samples: strips 16 × 2 mm^{-2}. $\dot{\varepsilon} \sim 0.01$ min^{-1}. *Designation from ref 26.

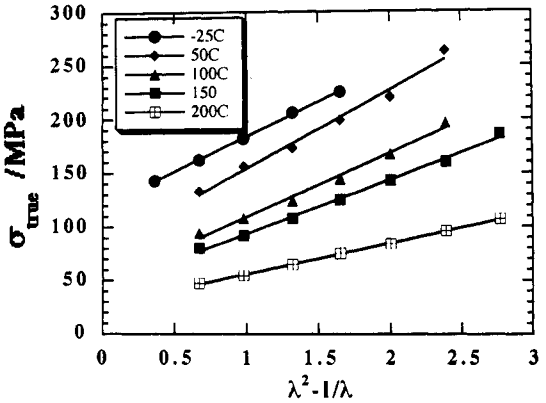

Figure 6. Gaussian plots for polyimide DPO.

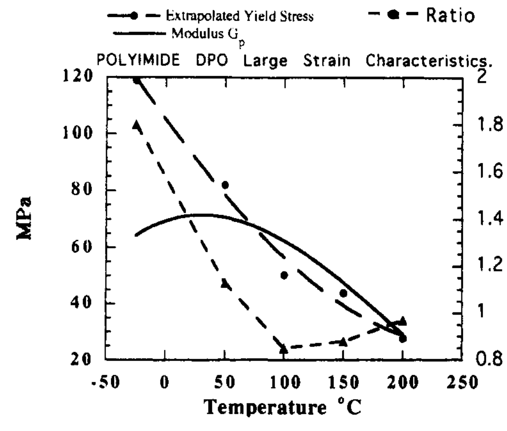

Figure 7. Gaussian constants for polyimide DPO.

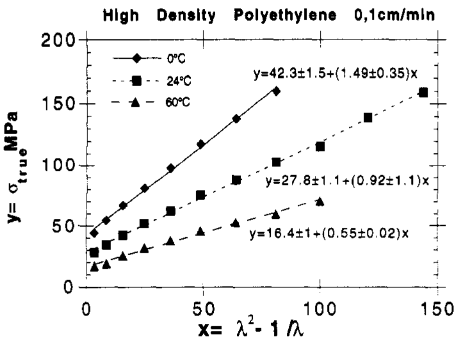

Figure 8. Gaussian plots for HDPE from the work of Meinel and Peterlin.[29]

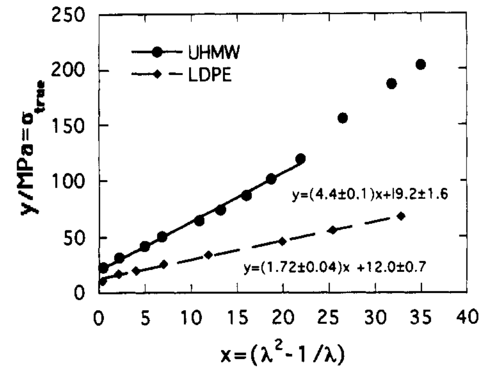

Figure 9. Low-density polyethylene and ultrahigh molecular weight polyethylene.

therefore possible to transform engineering stresses into true stresses. The results are given in Figures 5–7. It will be seen that after elimination of a rather large Hookean strain (0.08), the results for plastic strain for $\lambda > 1.12$ (i.e., 1.2–0.08) give good agreement with the Gaussian model. These measurements make it possible to estimate the quantities of interest, viz., the extrapolated yield stress Y, G_p, and the ratio Y/G_p over a wide range of temperatures as shown in Figure 7.

3.4. Polyethylene and Polypropylene. 3.4.1. High-Density Polyethylene (HDPE). Good Gaussian lines have already been presented from the original work of G'Sell and Jonas[1] with HDPE[21] as in Figure 2. A similar linear relation[3] has also been derived by G'Sell and Jonas from the curves shown in Figure 3. As both studies are based on the same experimental technique, it is of some interest to examine results for HDPE from other sources.

Suitable data are available from the work of Meinel and Peterlin[29,30] when they reported some of the first measurements of true stress–strain curves. These were obtained by the use of benchmarks to follow the extension process as it passed through the neck and, therefore, include an even wider variation in strain rate than occurs under conditions of uniform deformation. Their measurements, which have been treated as previously described, are presented in Figure 8 using the results at the lowest strain rate at temperatures of 0–60 °C. The lines which follow eq 1 quite well nevertheless show a slight convex curvature at medium strains, which could be due to the acceleration of the strain rate as the material travels through the neck. All the same, it should be noted that the points at 24 °C give a good linearity up to λ values of 12. Both Y and G_p fall as the temperature is raised, but their ratio remains sensibly constant at 29.2 ± 1.0 MPa.

Meinel and Peterlin also give results at 90 °C where a Gaussian plot exhibits a good deal of curvature at low values of λ. As with polystyrene (Figure 4), the temperature may be too high for the assumptions of the theory. However, for $6 < \lambda < 13$ a reasonably linear plot can be obtained with $G_p = 0.32$ MPa and $Y = 16$ MPa.

3.4.2. Low-Density Polyethylene (LDPE). A true stress–strain curve is included in Figure 3, and this was used to provide a Gaussian line by G'Sell and Jonas in ref 3. However, their plot only employed part of the experimental curve with λ values up to 3.2, and in Figure 9 a line covering the whole curve up to λ values of 6 is given. The fact that a good line is obtained over the whole length of the curve clearly increases the significance of the results, and the difference in G_p which is 1.7 MPa compared to 2.2 MPa for ref 3 is largely due to this factor.

Results for low-density ultrahigh molecular weight linear (UHMW) polyethylene are also plotted in Figure 9, and

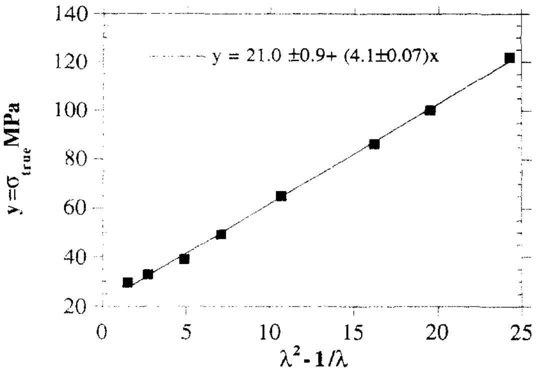

Figure 10. Gaussian plot for polypropylene. Points derived from ref 4.

these require some explanation. This polymer has a molecular weight an order of magnitude higher than that of normal, commercially processable materials and has to be formed by compression molding. A study of the molding variables[31] showed that the density and crystallinity of the molded test piece could be substantially controlled by the pressure and rates of cooling employed during molding. When the mold was quenched in ice water, a density as low as 0.928 g/cm^3 could be produced, which was very low for a polyethylene without short-chain branches. If the polymer had been within the range for commercially processable materials, its density would have been above 0.95. Prepared in this way, the polymer gave nearly uniform extension so that the curves obtained were suitable for a Gaussian plot (Figure 9).

The figure shows that the UHMW polymer gives a satisfactory linearity up to a λ value of about 4, but above this extension, the stress rises well above predicted levels. The departure from linearity at high strains could be ascribed to a "Langevin effect" with highly entangled chains but is more likely to be due to crystallization. Meinel and Peterlin showed that further crystallization and thickening of crystals took place during uniaxial extension and this effect could be greater with the UHMW polymer because of its low initial density. Both changes would increase the yield stress.[32,33] The increased value of G_p may be ascribed to the very high molecular weight which has already been shown to intensify strain hardening by Coates and Ward[34] and others.[18]

3.4.3. Polypropylene (PP). The improved technique described by G'Sell et al. in ref 4 provides a true stress–strain curve over a wider range of λ than that previously reported for polypropylene and reproduced in Figure 3. The later result generates the Gaussian plot shown in Figure 10 which extends to λ values of 5 and is therefore more significant than the more limited results which G'Sell and Jonas presented previously[3] (see Appendix I, Table AIB).

3.5. Poly(vinyl chloride) (PVC). Good Gaussian plots have already been obtained from measurements by Cross and Haward,[5] measurements by G'Sell and Jonas,[3] and, with more scattered points, early measurements by Vincent.[21,35]

3.6. Polymers with Extended-Chain Conformation. It has already been noted that the cellulose esters characteristically give uniform deformation in a tensile test, a property which makes them convenient for studying stress–strain curves. Unfortunately, many of them break at low values of λ, e.g., $\lambda < 1.5$. However, Levita and Struik[36] have published a true stress–strain curve for cellulose acetate butyrate (CAB) showing an extension up to $\lambda = 1.9$. This gives a good Gaussian plot (Figure 11). A short plot for a cellulose nitrate sheet, taken from ref 18, is shown in Figure 12 together with that for an amorphous copolymer of ethyl and propyl isocyanate.

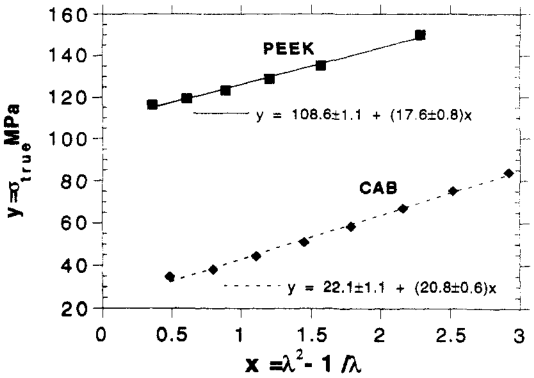

Figure 11. Gaussian plots from ref 4 (PEEK) and ref 36 (CAB).

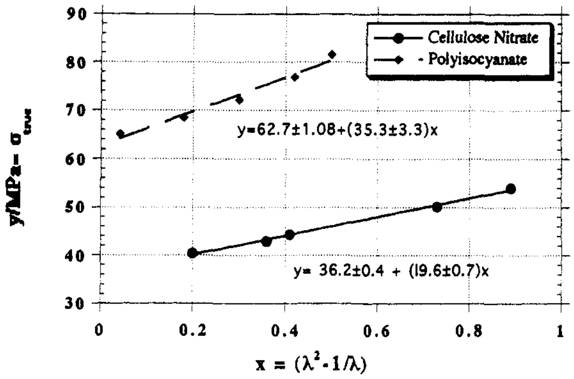

Figure 12. Graphs demonstrating the high values of G_p for polymers with a high Kuhn length.

The latter is of particular interest. It formed part of a series of isocyanate polymers and copolymers with the general formula $(-N(R)C(O)-)_n$ which were prepared and previously evaluated.[37,38] They were chosen because they were known to have a highly extended chain conformation.[39-41] It was found that all the polyisocyanates, whether crystalline or not, gave uniform extension in a tensile test. This particular copolymer was selected because it was amorphous and had a high yield stress, which was increased by working at 0 °C. It was believed that these factors would maximize the likelihood of necking, and therefore increase the significance of the observations that extension was uniform.

It should be noted that the polymers in Figure 12 give only small extensions. In the case of the isocyanate, λ only just exceeds 1.2. Therefore, although reasonable lines are obtained providing indicative values of Y and G_p, they do not add substantially to the evidence that the Gaussian plots are linear up to high values of λ, which is an important feature of some of the other graphs presented here.

Results from ref 4 for poly(aryl ether ether ketone) (PEEK) are also included in Figure 11 mainly for convenience. It may well have a more extended-chain conformation than, for instance, the vinyl polymers, but so far firm evidence is not known to have been published.

4. Discussion

4.1. Validity of the Gaussian Model. The method of evaluating a scientific hypothesis against experimental results produced for other purposes has some limitations. Experiments cannot be repeated to derive error bars or to clarify differences between observed and theoretically expected results. Nevertheless, in the course of this and previously published studies[3,5,6,21,25,42] in which the Gaussian equation has been applied to experimental data from a variety of sources which used different experimental techniques,[3,5,6,21] some 30 different examples of true stress–strain curves have been investigated and of those only a small minority have failed to comply reasonably well with the Gaussian equation. In some cases the agreement has been excellent. The significance of these results will now be discussed and, to this end, a table listing measured values of Y and G_p is given in Appendix I. Those cases where straight lines were not obtained is listed in Appendix II. Thus the evidence that the Gaussian equation gives a good representation of most true stress–strain curves is very strong.

4.1.1. Beginning Effects. As previously discussed, the model provides for the representation of the initial Hookean deformation ϵ_H by a simple linear modulus. In the form in which it was originally applied by Haward and Thackray[18] it is also capable of describing the gradual transition from elastic to plastic strain as the latter approaches the imposed strain rate. However, this complication has been avoided here by omitting measurements at low values of λ in order to simplify the presentation of results. The model does not, however, provide for any other special effects which may occur at the beginning of the large deformation process. For example, it predicts that there could never be a maximum in a true stress–strain curve. In fact, stress maxima are often observed at λ values of 1.05–1.30 and two features have been identified which can account for them.

The best documented feature is that due to the annealing (physical aging) of glassy polymers at temperatures immediately below T_g. The changes which take place result in an energy deficit, observable by differential scanning calorimetry (DSC) which generates an initial peak in the stress–strain curve. This peak provides additional mechanical energy which generally removes the deficit before steady deformation sets in.[15,16,43] The annealing effect, which can also be brought about by slow cooling after processing or even by prolonged storage, can be eliminated or greatly reduced when the sample is quenched in ice water from above T_g.[5] In some cases, e.g., with PVC,[44] polycarbonate,[16] and poly(ethylene terephthalate) (PET),[45] the increase in yield stress after annealing can considerably exceed 10%, and in such cases it promotes plastic instability necking and embrittlement.[43] The same effect also promotes shear bands which are not subject to geometrical magnification as in a conventional tensile test and are therefore uniquely dependent on true strain softening.[28,46] Thus the polymers which characteristically give shear bands, such as poly(methyl methacrylate),[46] polycarbonate,[47,48] and PET,[45,46] generally fail to comply with the Gaussian equation. The annealing effect may be related to volume contraction or other internal energy changes, such as the distribution of rotational isomers which have been linked to physical aging with PVC.[49] This accords with computer simulation studies which have shown that changes in rotational isomer distribution can occur at times and temperatures below those at which changes in the overall chain conformation take place.[50] Quite large changes in rotational isomer distribution have been observed at the early stages of plastic deformation with styrene polymers[14] and PET,[51] which will entail both internal energy and frictional losses and are clearly capable of generating a local maximum at the beginning of a stress–strain curve. Such effects appear to be characteristic of the glassy state. According to G'Sell,[2] true strain softening does not occur with crystalline polymers.

More recently, other internal energy effects have been reported by Oleynik et al.,[14] who made accurate calorimetric measurements during compression tests and related Q, the heat generated, to E, the applied mechanical work. They recorded substantial energy deficits which they related to "plastic shear defects" which acted as energy sinks and were considered to be a prior requirement for plastic deformation. These would inevitably augment the stresses required at the first stage of the process. Later, according to Oleynik's measurements $\mathrm{d}Q/\mathrm{d}E$ tends toward unity and the stored energy levels out at λ values above 1.2–1.3.

Here it should be noted shortly that, apart from the Hookean strain which is endothermic,[52–54] the Gaussian model deals only with frictional and entropy effects and therefore requires that all the applied energy appears as heat. Although there is a dearth of accurate calorimetry at high strains, the results available do show that most of the applied energy appears as heat.[52,55,56] Any changes in rotational isomers, such as have been observed or predicted during the main deformation process,[50,57] would inevitably have some influence on this conclusion.

4.1.2. Limit on Chain Extensibility. As indicated previously, the possibility remains that during the test the polymer chain will approach its full extension between the effective entanglements and the stress will rise above that predicted by the Gaussian equation. In such cases, the Langevin treatment, which gives a higher stress at the highest strains, may be more appropriate.

4.1.3. Changes in Crystallinity. In view of the many changes in crystal form which take place during plastic deformation, it is remarkable that the Gaussian relation can be usefully applied to crystalline polymers. Nevertheless, since an increase in the amount of crystallinity normally leads to a significant increase in yield stress, it is apparent that where large changes of this type take place during deformation they should affect the form of the stress–strain relation, as previously discussed for polyethylene.

4.2. Polymer Structure and G_p. A list of all the Gaussian constants presently available, other than those for polyethylene which is given in the text, is shown in Appendix I. The results are divided into three groups—extended-chain polymers, crystalline polymers, and amorphous polymers—and their significance will now be discussed.

4.2.1. Possible Analogy between Plateau Modulus $G_N°$ and G_p. The technology of elastomers and the theory of rubber elasticity both depend on the introduction of permanent chemical cross-links between the polymer chains.[19] However, according to the present proposal it is possible for a thermoplastic to exhibit rubberlike properties in the absence of chemical cross-links. Similar considerations apply to the plateau modulus $G_N°$ which measures the elasticity of a polymer melt above its softening temperature. Thus, in principle, both $G_N°$ and G_p should be determined by the decrease in configurational entropy as polymer chains assume a less random form. In each case, the entropy change takes place through the distortion of the macromolecular coil as restricted by interference between separate polymer chains ("entanglements") in the absence of chemical cross-links. However, both the definitions of the two constants and the methods of measuring them are quite different. The plateau modulus is determined by relaxation experiments using small deformations at relatively high temperatures

Table I

(a) Plateau Modulus $G_N°$ of Polyethylenes[a]

material	temp (°C)	$G_N°$ (MPa)	M_e	ref
14.5% ethyl groups[b]	110–220	1.2		59
polyethylene	100	2.7		59
polyethylene	190	1.6	1850	60
4% ethyl[c] branches	190	1.1–2.7	1250	61
polyethylene	190	2.1		62

(b) Strain Hardening Modulus and Extrapolated Yield Stress of Polyethylenes

material	temp (°C)	Y	G_p (MPa)	M_e	ref
LDPE	22	*d*	1.52, 2.2[e]	850–1360	6, 42
LDPE[f]	21	11	2.2		3
this paper[g]	21	12	1.72	1320	2
HDPE[h]	21	25	2.4		1, 21
HDPE	21	28	2.4		3
HDPE	0	42.3	1.49	1440	29
this paper	29	27.8	0.92	2550	
	60	16.4	0.55	4770	
	90	12.0	0.32	8200	

[a] Hydrogenated polybutadiene. [b] $G_N°$ not much affected by temperature. [c] Value of $G_N°$ considered more reliable than that of ref 60. [d] The method used requires a long extrapolation and is not accurate for the measurement of Y. [e] G_p increases with molecular weight (melt index falls); see UHMW polyethylene (Figure 9). [f] From original measurements. [g] Derived from the same curve as *f* but uses λ values up to 5.8 instead of 3.2. [h] From ref 1 at lowest strain rate. See Figure 2.

and frequencies.[58] So $G_N°$ is a rubbery modulus controlled by entanglements permanent only with small strains and short times. It is measured above the softening temperature, i.e., above T_g and T_m. The methods used employ relatively high frequencies and small strains, as under these conditions the use of larger strains and longer times generally causes permanent flow. G_p, on the other hand, is measured in the solid state, well below the softening temperature, and employs very large strains which are reversible only when the material is heated above its softening point (T_g or T_m). In each case, a modulus is measured which is assumed to be controlled by entanglements permanent under the conditions of testing. So, according to the conventional theory of rubber elasticity,

$$G_N° \text{ or } G_p = \rho \frac{RT}{M_e} \tag{4}$$

For some time now studies concerned with $G_N°$ have stimulated the application of elasticity theories to a condensed material consisting of free polymer molecules. It is therefore of interest to consider how this work may be related to G_p. This will now be discussed, starting with the case of polyethylene where a number of experimental results are available.

4.2.2. Polyethylene. The plateau modulus of polyethylene is determined at a high temperature, typically 190 °C. According to eq 4 M_e is proportional to ρRT, so that if M_e was constant G_p would be lower than $G_N°$ and the value of G_p measured at a lower temperature at constant M_e would be reduced. Taking densities of 0.76 g/cm^3 (190 °C) and 0.92 g/cm^3 (23 °C), the reduction factor would be 1.30 without making specific allowance for crystallinity below the melting point. Published values of $G_N°$ and M_e for polyethylene together with those for G_p and M_e from the Gaussian equation are given in Table I.

It will be seen at once that the actual values of $G_N°$, G_p, and M_e are remarkably similar. This may in part reflect the fact that the amorphous phase in polyethylene is always well above T_g, but G_p increases at lower temperatures and certainly does not extrapolate to $G_N°$ as the temperature is raised. It is hard to avoid the conclusion that G_p contains a frictional factor absent in $G_N°$ which determines the efficiency of entanglements.

Table II. G_p and $G_N°$ Values for Polystyrene and Poly(methyl methacrylate)

	$G_N°$ (MPa)	G_p (MPa)
polymer		
polystyrene	0.20[a]	2.2,[b] 0.56[c]
poly(methyl methacrylate)	0.48–0.62[a]	2.0[d]

[a] Reference 62. [b] Reference 7, from crazing studies at normal temperatures. [c] At 96.4 °C. [d] Reference 17, p 732, Figure 16. Procedures of the IUPAC Symposium, Prague, July 1992; *Makromol. Chem.* (to be published).

4.2.3. Polystyrene and Poly(methyl methacrylate). In Table II, G_p and $G_N°$ values are compared for polystyrene and poly(methyl methacrylate), which may be taken as typical of carbon chain polymers. It will be seen that the values of G_p and $G_N°$ differ substantially, as appears to be the case where measurements are available for other polymers. The higher values of G_p would of course lead to lower values of M_e than those derived from $G_N°$, and this subject will be discussed later.

4.2.4. Comparison of G_p between Different Types of Polymers. Any attempts to compare G_p between different polymers encounter the problem that G_p varies with temperature and that there is no theoretical basis for selecting appropriate temperatures. However, it is clear that G_p rises as the temperature falls, which is exemplified by the results for polyimide DPO and HDPE. This is also in agreement with the work of Baer et al.[63,64] who measured nominal stress–strain curves for polycarbonate over a wide range of temperatures and observed increases in strain hardening as the temperature was reduced. It must therefore be concluded generally that both G_p and Y increase as the temperature falls, and since Y is assumed to represent the frictional forces during deformation, it would be logical to compare values of G_p between different polymers at constant values of the yield stress. Alternatively, practical comparisons might be made over the range of temperatures at which the polymers are used. Accordingly, we may note that the value of G_p for polyimide changes from about 25 to 100 MPa over the temperature range +200 to −25 °C while Y goes from 30 to 120 MPa. Similarly, Peterlin's HDPE has G_p values which increase from 0.5 to 1.5 MPa as the temperatures fall from 60 to 0 °C and the yield stress from 16 to 42. Thus, at a value of $Y = 40$, G_p is about 1.4 for polyethylene and 50 for polyimide so there is no doubt that G_p values differ very significantly between different polymers when either of the above criteria are applied.

4.2.5. Extended-Chain Polymers and Polyimide. The first three polymers in Table AI of Appendix I are all known to have a high Kuhn length (A), which indicates that they have a high end-to-end distance and a low degree of tortuosity. Particular interest attaches to the cellulosics and the isocyanates. The former comprise different esters, such as acetate, nitrate, and butyrate, and ethers, such as ethyl cellulose, which may be used with varying quantities of plasticizer or none, but in all cases the stress–strain curve has a similar form. After a small maximum at yield, strain hardening starts at low values of λ (e.g., 1.1) and uniform deformation takes place. Similarly, all the polyisocyanates deform uniformly[37,38,66] with marked strain hardening which is unaffected by the nature of the side group or by crystallinity. These results support the proposition that strain hardening is determined by the main-chain backbone and the groups immediately attached to it. Values of the Kuhn length (A) have not been reported for the polyimides, but Argon and Bessonov[65] have published stress–strain curves for several different polyimides and have related "hinge length", i.e., the length of rigid-chain units between flexible linkages, to strain hardening. It would be reasonable to expect that the relatively large hinge length associated with polyimide DPO would generate a high value of A. In any case, all four polymers in Table I have high values of G_p and low values of the ratio Y/G_p (well below 3), which corresponds with their property of giving uniform deformation.

Other work supporting a correlation between Kuhn length, hinge length, and strain hardening comes from work on polyarylates.

It has been shown that where aromatic groups within a polymer chain are joined by an ester group in the p position, internal rotation does not result in any marked coiling of the polymer chain.[67] Thus the insertion of terephthalate moieties into a conventional polycarbonate chain should increase hinge length. Work by Aharoni[41] and by Prevorcek and de Bona[68] has demonstrated that the introduction of a terephthalate group is associated with an increase in the Kuhn length. The latter have also shown that there is an increase in the plateau modulus. Other workers using substantially similar copolymers have observed an increase in strain hardening as terephthalate units are introduced,[69,70] while adipate and sebacate units have the opposite effect.[71] These results are qualitatively in agreement with the other conclusions presented in this paper although neither the proposed deformation model (Figure 1) nor the Gaussian model has been assumed in the argument.

4.3. Relation of G_p to Present Concepts of Entanglement. Apart from polyethylene, the reported values of G_p are higher than the available figures derived from the plateau modulus. When substituted into eq 4, they generate figures for M_e which are low and generally unacceptable in terms of rubber elasticity theory. To take an extreme case, with a value of $G_p = 70$ and density 1.37 for polyimide DPO, we get $M_e = 48$ which is notably less than the repeat unit on the polymer chain, as previously observed with PEEK.[42]

One way of escaping from this dilemma is to base eq 4 not on the Gaussian theory but on the different and more general assumptions of Rivlin[72] and Mooney[73] as proposed in ref 5. Although this approach is perfectly valid, it offers no insight into the influence of polymer structure. This is important as strain hardening is a general property of thermoplastics and entails fresh criteria for their evaluation. Even if the Gaussian derivation were abandoned, the problem would not disappear. For example, in the Langevin procedure it was necessary to assume a very low value of 1.7 for the number of statistical links between points of entanglement for cellulose nitrate,[18] and this can hardly be reconciled with conventional random-chain statistics. Similar problems have been encountered for polycarbonate by Dettenmeier and Kausch[74] and discussed by Duckett.[75]

Fortunately, the study of the plateau modulus is already leading to a reassessment of the concept of entanglements. For example, Graessley and Edwards[62] have proposed that $G_N°$ is controlled by the total interaction between polymer chains, as determined by the contour length per unit volume, and the Kuhn length. Later, Edwards and Viglis[76] argued that when the polymer is cooled below T_g the chain is "pinched" at a series of points along its length, thus reducing extensibility (and therefore intensifying the strain hardening effect). This argument would invalidate eq 4 and support the previous conclusion that G_p is influenced by a viscous or frictional factor. Qualitatively, however, these newer concepts of entanglement are in line with the results in this paper, which also show G_p increases with more extended-chain configurations. In the same way, entanglements when regarded simply as uncrossable junctions of polymer chains will *increase* with stiff linear chains and the greater interpenetration of polymer coils.[62]

4.4. Plastic Instability and Toughness. The use of the Gaussian equation enables the Considere condition for plastic instability and necking to be partially quantified.[21] The polymers in Table AIA in Appendix I all have values of $Y/G_p < 3$ and none of them neck. Similarly, the polymers well-known to neck in a conventional tensile test have values well above 3. These include the polyamides, PET, PEEK, and HDPE.

On the other hand, when the ratio is just above 3, the mode of deformation becomes variable and easily influenced by other factors. Quenched UHMW polythene at low strain rates gives practically uniform deformation with a ratio of 4.4 but starts to neck if the strain rate is raised. With rigid PVC, quenching and a low strain rate gives uniform deformation with a ratio of 2.9, but normal materials and strain rates always neck. For example, the other two PVC materials listed in Appendix I gave ratios of 3.6 and 5.0. Generally, it seems that the Considere condition needs to be somewhat exceeded if a distinct neck is to be formed.

Electron micrographs of the crazing structure which preceded brittle fracture in polymer glasses show that they consist of an assembly of micronecks[77,78] for which the Considere condition should also apply. In other words, a high value of the ratio Y/G_p. This is entirely in line with Kramer's detailed study of craze structure and formations[7,20] which showed that crazing was promoted by a high value of λ_{max}, i.e., a high value of Y/G_p. He also showed that when strain hardening was enhanced by preorientation of the material, crazing was less easily induced or even suppressed entirely.[79] It will be seen from Table AIC that the three styrene polymers which characteristically undergo crazing and brittle fracture have low values of G_p and very high values for Y/G_p.

Conclusions

(1) Most of the available published true stress–strain curves for thermoplastics have a major plastic component which is well represented by eq 1.

(2) This equation corresponds to a model in which a spring and dashpot are in parallel, and the spring responds in accordance with the Gaussian network theory of rubber elasticity.

(3) The slope of the Gaussian line provides a strain hardening modulus G_p which increases as the temperature falls.

(4) In accordance with the Considere principle, the ratio Y/G_p broadly determines whether the polymer extends uniformly or necks.

(5) According to conventional theory, the constant G_p may be used to calculate entanglement moleclar weight M_e. For polymers with high values of G_p the results are unacceptably low.

(6) Polymers with highly extended chain conformations (high values of Kuhn length) have high values of G_p.

Appendix I

Values for Y, G_p, and Ratio Y/G_p for thermoplastics are given together with estimates of Kuhn length A.

Table AI

material	Y	G_p (MPa)	ratio	temp (°C)	A (AU)[41]
(A) Polymers with High Values of the Kuhn Length (A)					
cellulose acetate butyrate[36]	22.1	20.8	1.06	23	160[a] 198[b]
cellulose nitrate[18]	36.2	19.6	1.85	23	178
ethyl, propyl isocyanate[37,38]	62.7	35.3	1.88	0	1000[c]
polyimide DPO	82.0	73.0	1.13	50	*d*
(B) Crystalline Polymers[e]					
polyamide 6[f]	82.2	11	7.5	21	9.4
polyamide 6[g]	(77.5)	(1.4)	(6.8)	21	9.4
polyamide 66[f]	97.4	16.8	5.8	21	10.6
polyamide 66[g]	(100.3)	(16.3)	(6.2)	21	10.6
polypropylene[f]	35.5	4.2	8.5	21	11.1
polypropylene[h,i]	21.0	4.1	5.1	21	11.1
UHMW polyethylene[i]	19.2	4.4	4.4	22	
poly(oxymethylene)[i]	22.3	4.5	4.9	100	
polytetrafluoroethylene[f]	13.5	5.0	2.7	21	
poly(aryl ether ether ketone) (crystalline)[i]	108.6	17.6	6.2	21	
poly(aryl ether ether ketone) (crystalline)[42]	96.0	21.1	4.5		
(C) Glassy Polymers					
poly(tert-butylstyrene)[j,7,21]	70	1.3	54	room temp	
polystyrene[j,7,21]	70	2.2	32	room temp	16.9[31]
styrene–acrylonitrile copolymer[j,7,21]	160	3.4	47	room temp	
poly(methyl methacrylate)[25]	13.9	2.0	7.0	90	17[31]
rigid poly(vinyl chloride)[k,21]	50	10	5.0	20	11.9[31]
quenched rigid poly(vinyl chloride)[5]	38	13.2	2.9	23	11.9[31]
rigid poly(vinyl chloride)[l]	47.8	14.0	3.4	21	11.9[31]
rigid poly(vinyl chloride)[m]	(48.3)	(12.9)	(3.6)	21	11.9[31]
amorphous poly(aryl ether ether ketone)[42]	70	12.5	5.6		

[a] Cellulose acetate. [b] Cellulose butyrate. [c] *n*-Butyl isocyanate. [d] High hinge length.[65] [e] For commercial polyethylenes, see Table Ib (text). [f] Results obtained directly by the authors.[3] [g] Points derived from copying published curves,[2,25] i.e., original data as in *f*. [h] Results taken from ref 4. Differences in yield stress suggest that there were differences in the grade of polymer used. [i] This paper. [j] Measured from crazing studies. [k] Original points showed considerable scatter. [l] Original results from ref 3. [m] Points obtained by copying from ref 2 as indicated by brackets. Original data as in *l*.

Appendix II

Table AII. Summary of Unsuccessful Gaussian Plots[a]

material	observation	remarks
polycarbonate	large initial max	true strain softening extending to relatively high strains,[2] shear bands[48]
high mol wt PMMA at elevated temp	high initial peak	true strain softening,[4,17] shear bands at normal temp[46]
HDPE, 90 °C	straight line only between $\lambda = 6$ and 13	temp probably above limit for theory
polystyrene, 96.4 °C	significant curvature	temp too high

[a] With PVC there is a variable initial peak depending on thermal history which may or may not affect the rest of the stress–strain curve. After quenching, the material can give uniform deformation.

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