Strain Rate Sensitivity of Polymers in Compression from Low to High Rates

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Résumé. — Par des essais de compression uniaxiale à température ambiante (295 K) nous avons étudié la sensibilité à la vitesse de déformation de dix sept polymères différents entre 10^{-2} et 3×10^4 s^{-1}. L'étude d'un tel nombre de matériaux a permis d'identifier des comportements communs. Afin de minimiser l'effet des contraintes d'inertie radiales sur le seuil d'écoulement mesuré, la taille des éprouvettes a été diminuée aux vitesses de déformation les plus élevées. Des lubrifiants à base d'hydrocarbures ont été utilisés pour éliminer les contraintes de friction entre les échantillons et les barres à toutes les vitesses de déformation. Tous les polymères sauf trois (l'acétal, le polyéthylène de haute densité (HDPE) et le polytétrafluoroéthylène (PTFE)) ont présenté une relation linéaire entre là contrainte et le logarithme de la vitesse de déformation entre 10^{-2} et 10^3 s^{-1}, ceci avec un niveau de confiance élevé. L'accroissement de la température de l'éprouvette dû à la dissipation de l'énergie n'est pas suffisant pour expliquer les écarts à la linéarité observés dans les trois exceptions. La sensibilité à la vitesse de déformation ne dépend pas fortement de la déformation sauf pour deux matériaux (PTFE et difluoride de polyvinylidène (PVDF)). Pour dix des polymères étudiés on a observé un changement net de la sensibilité à la vitesse de déformation autour de 10^3 s^{-1}. Parmi ces dix, cinq présentaient un accroissement et cinq une *diminution* de la sensibilité au delà de cette vitesse de déformation. Les sept autres n'ont pas montré de changement notable de la sensibilité. Pour quelques uns de ces polymères qui ne présentaient pas de changement ou montraient une diminution de la sensibilité à la vitesse de déformation un minimum de résistance a été observé pour une vitesse de déformation de 10^4s^{-1}. Ce point n'est pas expliqué mais est significatif au regard de la précision des mesures. Les volumes d'activation calculés à partir de la sensibilité à la vitesse de déformation de la contrainte d'écoulement (ca. 10^{-21} m^3) sont plusieurs milliers de fois supérieurs au volume d'activation pour une molécule typique de polymère.

Abstract. — The strain rate sensitivity of the uniaxial compressive stress-strain response of seventeen different polymers at room temperature (295 K) has been investigated over the strain rate range $10^{-2} - 3 \times 10^4$ s^{-1}. The advantage of studying such a large number is that specific groupings of behaviour could be identified. The size of the specimens was decreased at the very highest strain rates to ensure that the contribution of radial inertial stresses to the measured yield pressure was minimal. Hydrocarbon based lubricants were used to eliminate frictional stresses between the specimens and the anvils at all strain rates. All but three of the polymers (acetal, high density polyethylene (HDPE), and polytetrafluoroethylene (PTFE)) exhibited a linear relationship between stress and log strain rate to a high degree of confidence over the strain rate range $10^{-2} - 10^3$ s^{-1}. The increase in specimen temperature due to plastic work dissipation

is not sufficient to account for observed deviations from linearity in the three exceptions. The rate sensitivity of all but two (PTFE and polyvinylidene difluoride (PVDF)) was found not to depend strongly on strain. Ten of the polymers studied exhibited a sharp change in rate sensitivity at a strain rate of around 10^3 s^{-1}. Of these ten, five showed an increase but five showed a *decrease* in rate sensitivity above this strain rate. The other seven did not show a clear change in rate sensitivity. Some of those polymers that either showed no change or a decrease in rate sensitivity also exhibited a dip in strength at a strain rate of 10^4 s^{-1}. This observation is not understood but appears to be significant based on the accuracy of the data. The activation volumes calculated from the rate sensitivity of the flow stresses (ca. 10^{-21} m^3) are several thousand times larger than the volume of a typical polymer molecule.

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1. Introduction.

This paper reports the results of a preliminary study of the mechanical properties of polymers deformed in compression under conditions of one-dimensional stress over a wide range of strain rates ($10^{-2} - 3 \times 10^4$ s^{-1}). There are two major reasons for carrying out such a study. First, it is important for engineers to have accurate data that they can use in calculating the response of structures made from these materials [1]. Second, the strain rate response can give information about deformation mechanisms at the molecular level [2-8].

In earlier work on the mechanical response of polymers at high compressive strain rates ($10^3 - 3 \times 10^4$ s^{-1}) at room temperature (295 K), we were not able to determine their rate sensitivity accurately as data were not available at moderate strain rates ($1 - 10$ s^{-1}) [9, 10]. In addition, we made the unexpected observation that the yield and flow stresses of many of the polymers studied *decreased* at strain rates in excess of 10^4 s^{-1}.

Since then, several improvements in our high strain rate experimental technique have been made, the most important being the redesign of the velocity measuring equipment on our Direct Impact Hopkinson Bar (DIHB) to obtain 0.5% accuracy. As reported in this paper, this has allowed us to quantify the differing responses of the yield stress of the various polymers to greater precision.

2. Theory.

For a material of a given type and microstructure, the stress σ it can support at a given pressure depends in general on the strain ε, strain rate $\dot{\varepsilon}$, and temperature T [11-13] i.e.

$$\sigma = \sigma(\varepsilon, \dot{\varepsilon}, T). \tag{1}$$

The functional form of this relation is the material's constitutive equation and is determined experimentally. In this study, the constraint we imposed on the specimens was to deform them at various different strain rates at room temperature (295 K). The effects of changing the ambient temperature and pressure were not investigated.

For many materials over a certain range of temperature, plastic deformation is an activated process in which the strain rate and stress can be related *via* the following simplified form of

the Eyring equation [14]:

$$\dot{\varepsilon}(\sigma, P, T) = \dot{\varepsilon}_0(\sigma, P, T) \exp[-\Delta G_{\mathrm{a}}(\sigma, P, T)/kT], \tag{2}$$

where ΔG_{a} is the Gibbs Free Energy for the process and k is the Boltzmann constant [3, 15]. This equation holds if only one stress-activated process is operating, and if the (forward) stress-activated processes are occurring much faster than the (backward) relaxation processes.

The various partial derivatives of the Gibbs Free Energy give the magnitudes of the molecular parameters involved in the deformation processes. The derivative of particular importance for this paper is that with respect to stress, for this gives the activation volume V_{a} for plastic deformation under uniaxial compressive stress:

$$V_{\mathrm{a}} = -\left(\frac{\partial \Delta G_{\mathrm{a}}}{\partial \sigma}\right)_{P,T}. \tag{3}$$

Substituting for ΔG_{a} from equation (2), we obtain:

$$V_{\mathrm{a}} = kT \left(\frac{\partial \ln(\dot{\varepsilon}/\dot{\varepsilon}_0)}{\partial \sigma}\right)_{P,T}. \tag{4}$$

It should be noted here that the interpretation of V_{a} is not straightforward [16]. It arises in plasticity theory as the product of a jump length multiplied by an area, the idea being that bulk plastic deformation arises as the sum of a large number of elementary and discrete motions of sections of polymer molecules [17, 18]. These sections are envisaged as jumping a certain distance along a tube with a cross-sectional area determined by the other molecules in the vicinity.

Experimentally what we measure is the reciprocal of $(\partial \ln \dot{\varepsilon}/\partial \sigma)_{P,T}$ at a given strain. This will give the activation volume if the stress dependence of the pre-exponential term $\dot{\varepsilon}_0$ of equation (2) is small compared to that of the exponential term (i.e. $\partial \ln \dot{\varepsilon}_0/\partial \sigma$ can be ignored), and if the state of the material depends only on the strain and not on the prior deformation history with respect to strain rate and temperature [3].

Various methods for checking the stress dependence of the pre-exponential in creep experiments are given in [15, 19-22]. These would be difficult to perform in high-strain rate testing. However, since the pre-exponential term does not depend exponentially on the stress (or its stress dependence could be incorporated within the exponential), a plot of stress against $\ln \dot{\varepsilon}$ for a given strain will not be linear if the pre-exponential has, say, a strong power-law dependence on stress. Briscoe and Nosker [23, 24] and Fleck *et al.* [25] found empirically that the simple Eyring approach outlined above is adequate to describe the high strain rate behaviour of polyethylene, PC and polymethylmethacrylate (PMMA).

3. Materials used.

The polymers used in this study are the same as in our previously reported work [9, 10]. Details of their thermal properties may be found there.

Stress-strain curves were obtained by compressing right circular cylinders of the polymers in four different machines to cover the required strain rate range. Cylinders of two different sizes (but with the same aspect ratio) were made for each polymer studied. The smaller of the two sizes were used at the higher strain rates to ensure that radial inertial stresses remained negligible at all the strain rates tested [9, 26-29].

Six polymers (nylon 6, nylon 66, polycarbonate (PC), noryl, polybutylene teraphthalate (PBT), and polyvinylidene difluoride (PVDF)) were available as injection moulded discs 5 mm in diameter and either 2 mm or 1 mm thick. An annular leather punch was used to make 2.5 mm diameter specimens from the 1 mm thick discs.

All the other polymers (with the exception of acrylonitrile-butadiene-styrene (ABS: see below) were obtained in rod form from which discs 2 mm and 1 mm thick were parted off on a lathe. Polyethersulphone (PES) and polyetheretherketone (PEEK) were kept in a dessicator until used, as were some specimens of nylon 6 and nylon 66. All other polymers were stored in the laboratory and were therefore subject to ambient humidity. Specimens 2.5 mm in diameter were punched out from the 1 mm thick discs using an annular leather punch. PES and PEEK proved too tough for this method, so a flat ended punch was used to make the smaller specimens of these polymers. A flat-ended punch was also used to make 5 mm diameter specimens from the 2 mm thick discs parted from rods.

ABS was purchased as 3 mm and 1 mm thick sheets. A flat-ended punch was used to make 6.35 mm diameter specimens from the larger sheet and an annular leather punch to make 2.5 mm diameter specimens from the thinner sheet.

4. Experimental method.

Four different machines were used in this study to obtain stress-strain curves in uniaxial compression over the strain rate range required. The lowest strain rates (10^{-2} s^{-1}) were obtained by compressing the larger specimens in a conventional screw driven Instron mechanical testing machine. The displacement of the specimen ends was measured by attaching two linear voltage displacement transducers to the steel anvils between which the specimens were deformed.

In previous work, we used candlewax as a lubricant. It was not, however, a perfect lubricant. However, when paraffin wax (a lower molecular weight hydrocarbon) was used as a lubricant, negligible difference was found in the maximum stress supported by 5 mm diameter discs of PC of two different thicknesses (Fig. 1). PC was used in this study because it has one of the highest unlubricated friction coefficients (0.4) of the polymers previously investigated [9], so that if a successful lubricant could be found for it, it would be likely to work for the others also.

The idea behind using discs of a given diameter and differing thicknesses is that the pressure p a cylindrical specimen exerts depends on its yield stress σ_y and the friction at its surfaces m through the following formula:

$$p = \left(1 + \frac{md}{3\sqrt{3h}}\right)\sigma_y, \tag{5}$$

where d is its diameter and h its height. If varying h does not alter the stress-strain curve, then $m = 0$ i.e. the lubrication is perfect and the measured pressure is the uniaxial yield stress.

The highest strain rates ($10^3 - 3\times10^4$ s^{-1}) were obtained in our two DIHBs, the larger having instrumented bars 10 mm in diameter, the smaller having bars 3 mm in diameter [10, 30, 31]. Both sizes of specimen were deformed in the larger of the DIHBs to obtain two different strain rates. Only the smaller specimens were tested in the smaller bar to obtain stress-strain curves at the highest strain rates reported in this paper (3×10^4 s^{-1}). Petroleum jelly (vaseline) was used as a lubricant as it had previously been found to give perfect lubrication in compressive high strain rate tests on polymers up to natural strains of about 0.4 [9, 10, 23].

Intermediate strain rates in the range $1 - 20$ s^{-1} were obtained by compressing the larger specimens in a hydraulic mechanical testing machine (Dartec M/1000) at two different cross-head speeds. Again petroleum jelly was used as a lubricant.
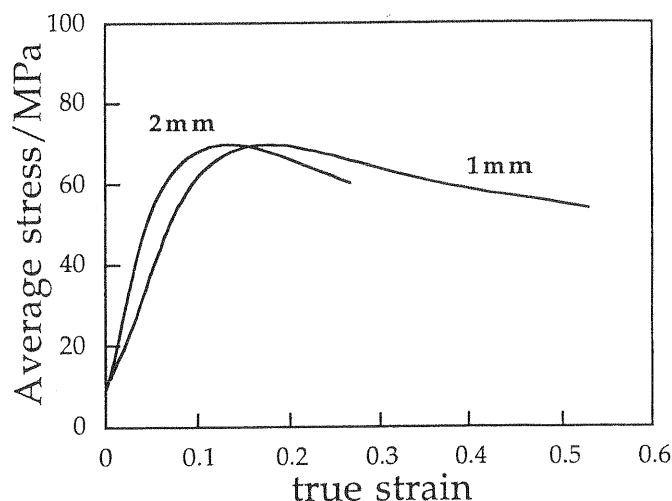
Fig. 1. — Stress-strain curves for 5 mm diameter PC specimens of two different thicknesses deformed in an Instron at strain rates of about 10^{-2} s^{-1} and lubricated by paraffin wax.

5. Results.

Stress-strain curves for all the polymers studied are presented in figure 2 up to strains of 0.6. The stress plotted is true stress i.e. the load divided by the current area of the specimen. The strain is natural compressive i.e. $\ln(h_0/h)$, where h_0 is the original height and h the current height of the specimen. Each curve is the average of four experiments, and the error in the strain rate quoted is the standard deviation.

It can be seen in figure 2 that the stress-strain curves do not go through the origin. There are several reasons for this. At low to medium strain rates a "bedding down" process occurs where the lubricant layer adjusts to the stresses imposed upon it. At high strain rates an additional factor comes into play due to the dispersion of the stress pulse propagating down the output rod to the strain gauge position. In both cases this leads to the measured force starting to rise *before* the specimen starts to deform. In addition none of the specimens are initially perfect right circular cylinders due either to mould shrinkage or distortion in the punching out process. The result of all these experimental errors is that the compressive Young's modulus of the specimens *cannot* be deduced from the stress-strain curves plotted. Thus in this work we only consider the rate sensitivity of the stress after the maximum in the stress-strain curves.

Several polymers exhibit pronounced load drops at all strain rates: noryl, PBT, PC, PES, PET, PP, PVC, PVDF. Others flow at nearly constant stress: ABS, acetal (or polyoxymethylene), the two nylons (moist and dry) and PEEK. HDPE shows some strain hardening before flowing at constant stress above a strain of about 0.3. PTFE, after yielding at a very low stress, is seen to exhibit the largest strain hardening effect of all the polymers.

Strictly speaking, the rate sensitivity should be obtained by plotting the stress against strain rate for material in the same microstructural state (strain is not a state variable [12, 32]). As it is usually impractical to measure this state variable during deformation, a macroscopic mechanical parameter has to be found that can be related to microstructure [33]. However, Wu and Turner [3] and G'Sell and Jonas [34] used strain rate jump tests to check whether polymers exhibit deformation history effects: they found no such effects were detectable for nylon 6, nylon 66, PC, HDPE, low density PE, PP, PTFE, or PVC up to strain rates of 10^{-1} s^{-1}.

As can be seen from figure 3 and table I, for most of the polymers studied (except for PTFE and PVDF), the rate sensitivity depends only weakly on strain (e.g. Fig. 3c). Thus normally only one set of data is plotted: the maximum stress. The justification for this is that although yield does not necessarily take place at the same strain for all strain rates, it is likely to occur when the polymer is in the same microstructural state. Graphs showing the rate sensitivity at more than one strain are included for a few polymers where the resulting lines are clearly separable. Error bars (equal in magnitude to the standard deviation of the data) are included
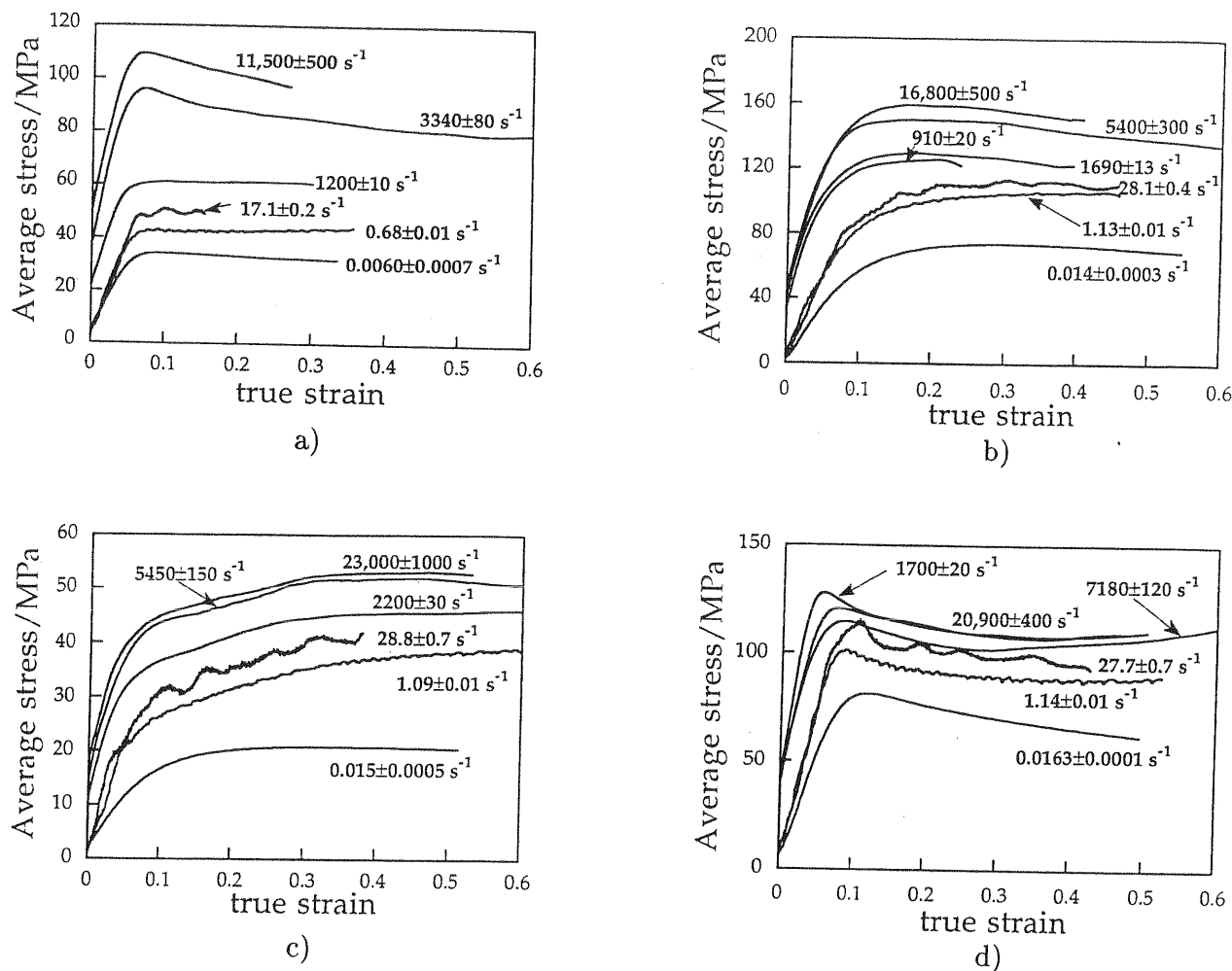

Fig. 2. — a) Compressive stress-strain curves for ABS at six different strain rates. b) Compressive stress-strain curves for acetal at seven different strain rates. c) Compressive stress-strain curves for HDPE at six different strain rates. d) Compressive stress-strain curves for noryl at six different strain rates. e) Compressive stress-strain curves for dry nylon 66 at six different strain rates. f) Compressive stress-strain curves for moist nylon 66 at six different strain rates. g) Compressive stress-strain curves for dry nylon 6 at six different strain rates. h) Compressive stress-strain curves for moist nylon 6 at six different strain rates. i) Compressive stress-strain curves for PBT at six different strain rates. j) Compressive stress-strain curves for PC at six different strain rates. k) Compressive stress-strain curves for PEEK at seven different strain rates. l) Compressive stress-strain curves for PES at seven different strain rates. m) Compressive stress-strain curves for PET seven different strain rates. n) Compressive stress-strain curves for PP at seven different strain rates. o) Compressive stress-strain curves for PTFE at six different strain rates. p) Compressive stress-strain curves for PVC at seven different strain rates. q) Compressive stress-strain curves for PVDF at six different strain rates.
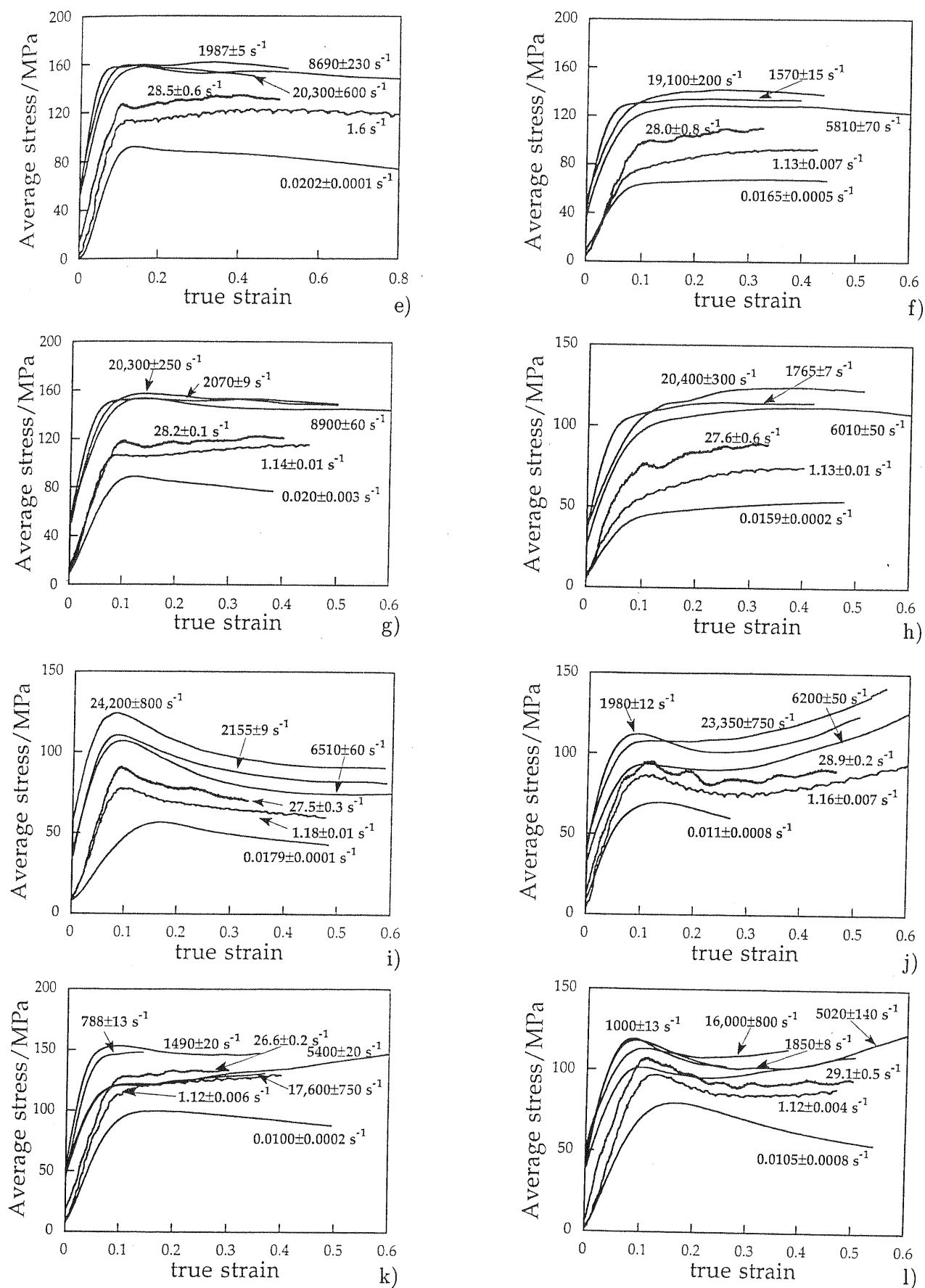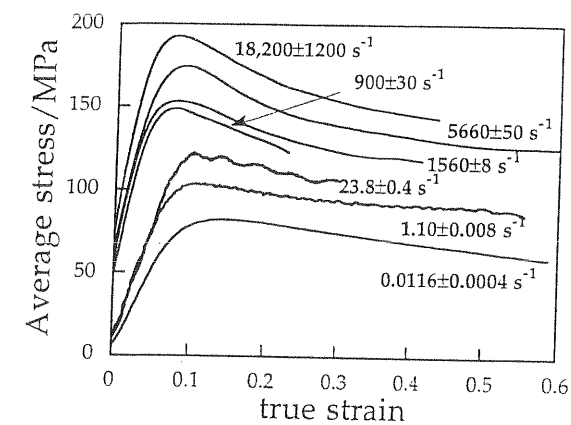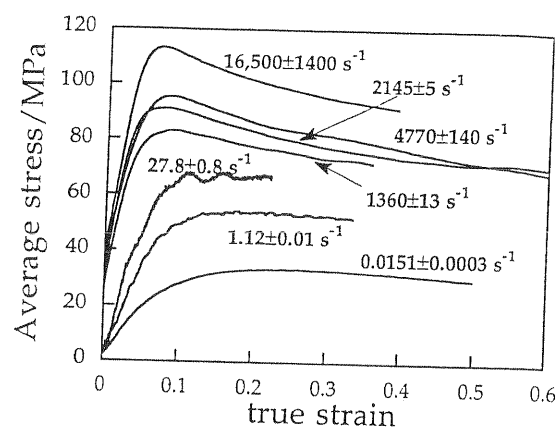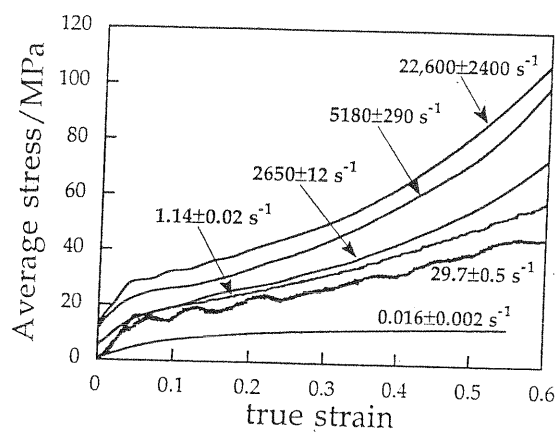
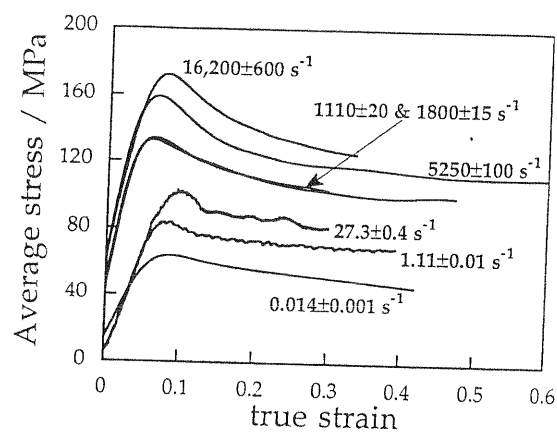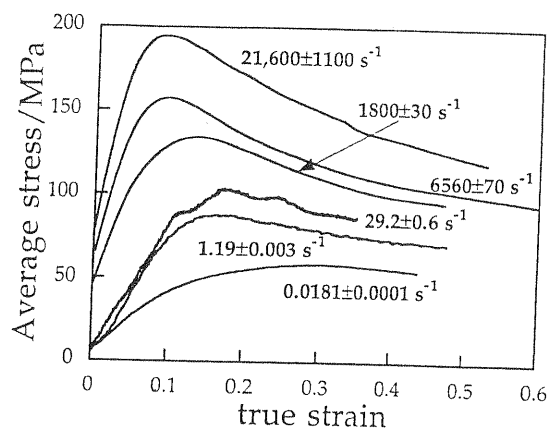Fig. 2. — *(continued)*

m)

n)

o)

p)

q)

Fig. 2. — (continued)

in figure 3 where only one line is plotted, but in most cases the error in the stress and strain rate is smaller than the symbol marking the data points. Table II gives the rate sensitivity at strain rates greater than 10^3 s^{-1} for those polymers showing bilinear behaviour.

Table III gives the maximum stresses (with standard deviation) for those polymers where at least some of the stress-strain curves show a maximum. Table IV gives the stresses at a natural strain of 0.2 for all polymers. By combining this information with the rate sensitivities in tables I and II, it should be possible to obtain reliable data for engineering use in modelling deforming structures.
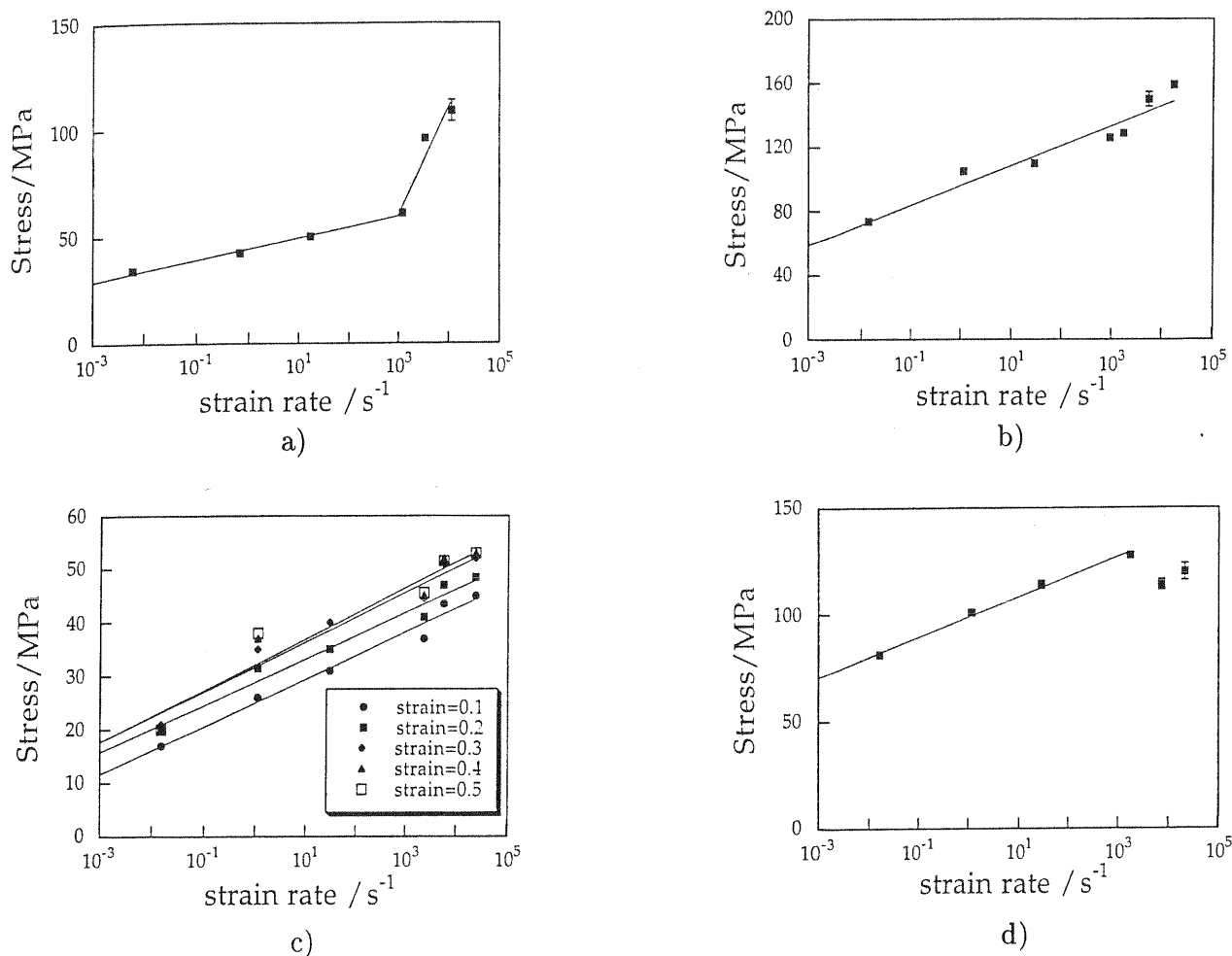

Fig. 3. — a) Plot of the maximum stress as a function of strain rate for ABS. b) Plot of the maximum stress as a function of strain rate for acetal. c) Plot of the stress as a function of strain rate for HDPE at five different natural strains. d) Plot of the maximum stress as a function of strain rate for noryl. e) Plot of the maximum stress as a function of strain rate for dry nylon 66. f) Plot of the stress at a natural strain of 0.2 as a function of strain rate for moist nylon 66. g) Plot of the maximum stress as a function of strain rate dry nylon 6. h) Plot of the stress at a natural strain of 0.2 as a function of strain rate for moist nylon 6. i) Plot of the stress as a function of strain rate for PBT at three different natural strains. j) Plot of the maximum stress as a function of strain rate for PC. k) Plot of the maximum stress as a function of strain rate for PEEK. l) Plot of the maximum stress as a function of strain rate for PES. m) Plot of the stress as a function of strain rate for PET at four different natural strains. n) Plot of the maximum stress as a function of strain rate for PP. o) Plot of the stress as a function of strain rate for PTFE at five different natural strains. p) Plot of the maximum stress as a function of strain rate for PVC. q) Plot of the maximum stress as a function of strain rate for PVDF.
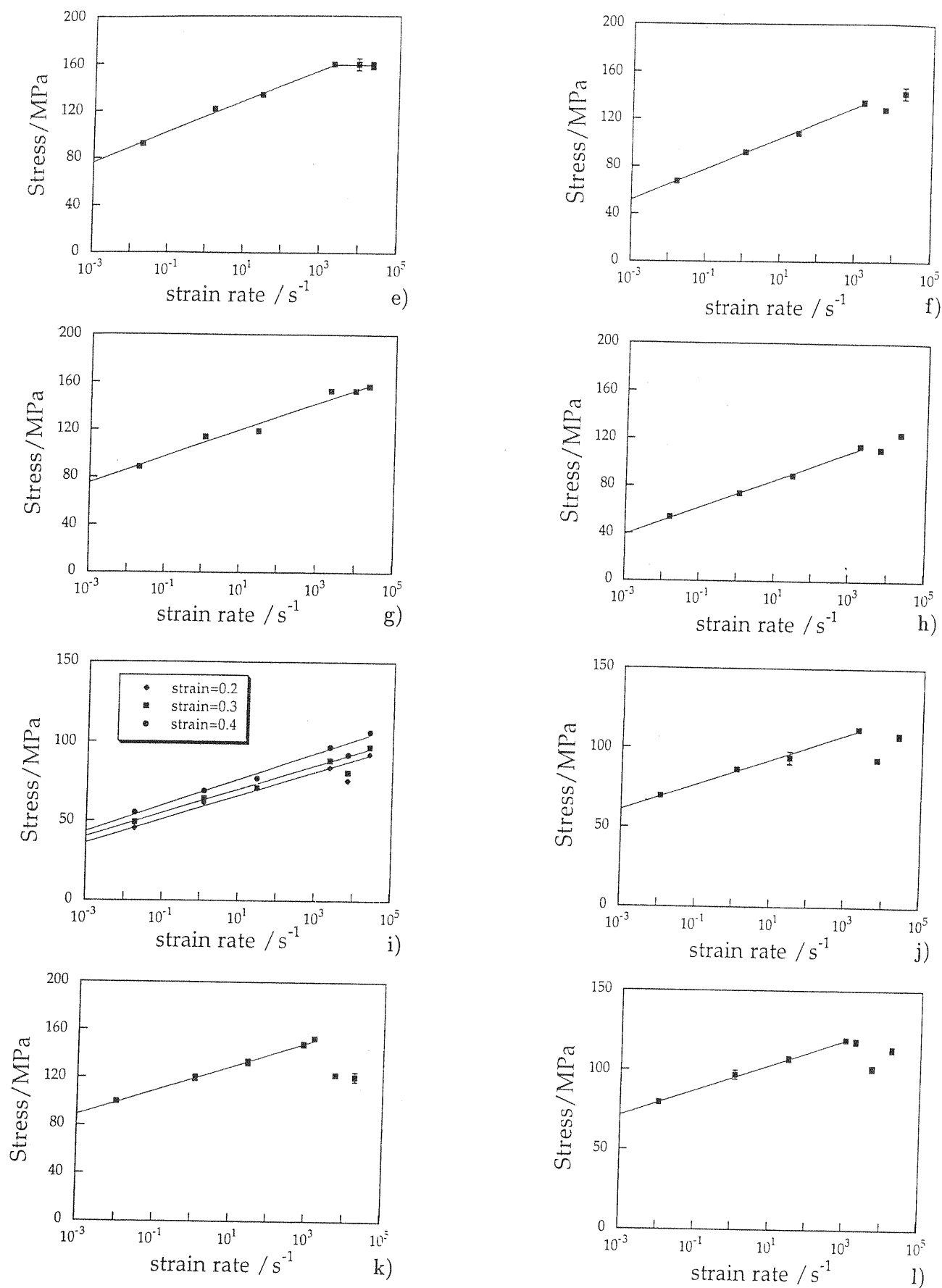
Fig. 3. — (continued)
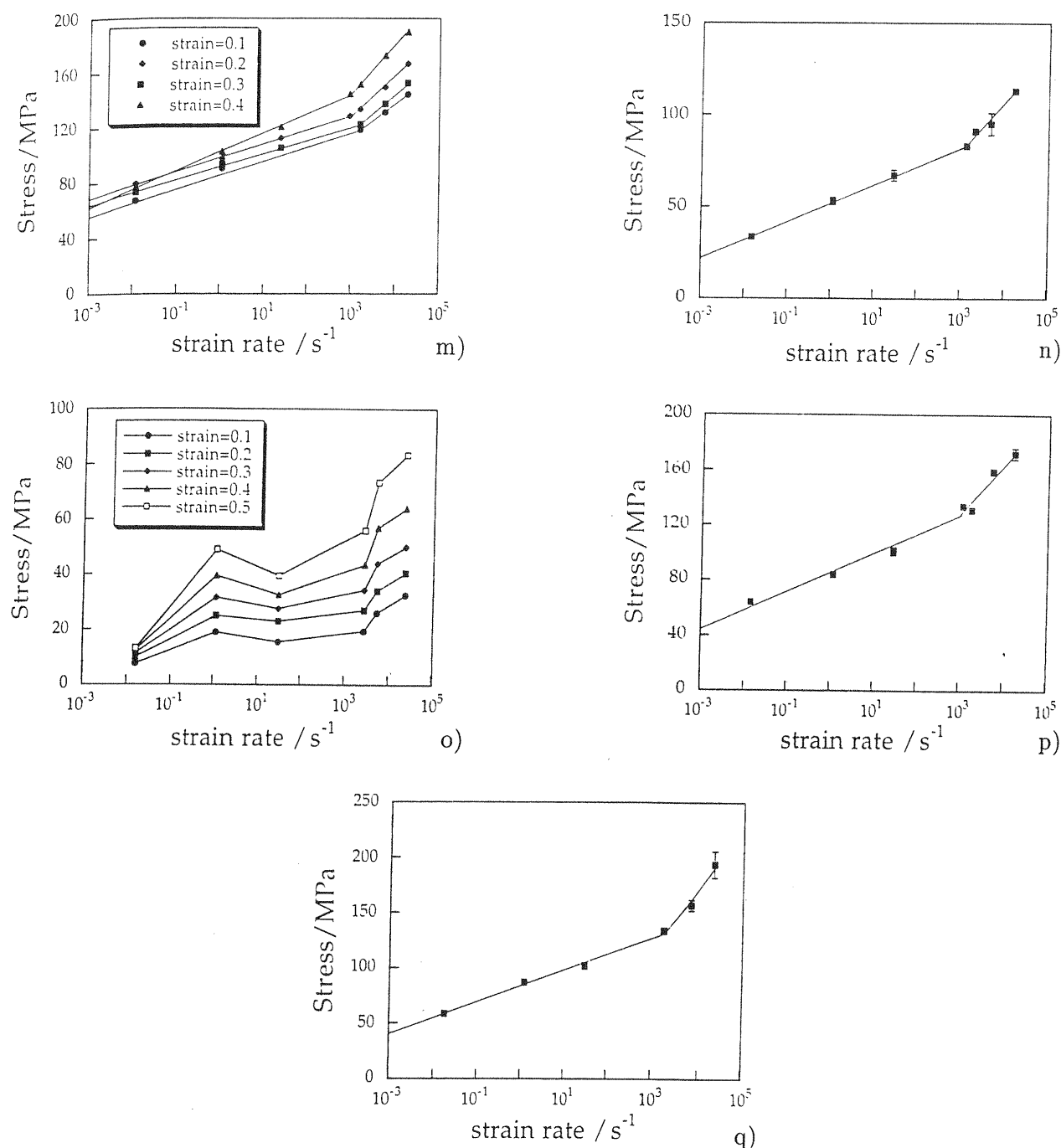
Fig. 3. — *(continued)*

Several different types of behaviour can be observed: (i) those exhibiting a bilinear relationship where the rate sensitivity of the stress *increases* sharply at a strain rate of about 10^3 s^{-1} (ABS, PET, PP, PVC, PVDF), (ii) those showing a *decrease* in stress supported above a strain rate of 10^3 s^{-1} (noryl, dry nylon 66, PC, PEEK, PES), (iii) those where the data do not unambiguously show a change of slope over the strain rate range investigated (acetal, HDPE, moist nylon 66, dry nylon 6, moist nylon 6, PBT) with the possible exception of acetal at a strain of 0.4, and (iv) PTFE. Several polymers from classes (ii) and (iii) show a sharp dip at 10^4 s^{-1} (noryl, moist nylon 66, moist nylon 6, PBT, PC, PEEK, PES). The arguments

Table I. — *Strain rate sensitivity parameter* $(\partial\sigma/\partial\ln\dot\varepsilon)/\mathrm{MPa}$ *for* $\dot\varepsilon = 10^{-2} - 10^{3}$ s^{-1}.

Polymer	Max. or flow stress	ε = 0.1	ε = 0.2	ε = 0.3	ε = 0.4	ε = 0.5	Notes
ABS	2.20	2.25	2.31	2.37	-----	-----	bilinear
Acetal	5.5	-----	5.7	5.3	-----	-----	ε = 0.4 data indicates two changes of slope
HDPE	2.0	1.9	1.9	2.0	2.05	2.1	no obvious change of slope
Noryl	4.02	3.5	3.23	3.26	3.59	-----	drop at high $\dot\varepsilon$
N66 dry	5.73	-----	6.01	6.30	6.33	6.17	-----
N66 moist	5.74	5.9	5.90	5.79	5.75	-----	-----
N6 dry	5.0	5.1	5.25	5.05	-----	-----	Possible slope change ε = 0.3
N6 moist	4.85	5.6	5.61	5.38	5.26	-----	Change at $\dot\varepsilon$ > 10³ s⁻¹ but no line
PBT	4.35	-----	3.4	3.0	2.9	-----	5th point off line
PC	3.41	3.48	2.97	3.74	4.23	-----	5th (or 4th) point dips
PEEK	4.37	4.96	3.84	4.1	-----	-----	drop at high $\dot\varepsilon$
PES	3.41	-----	2.30	2.76	3.25	-----	dip at high $\dot\varepsilon$ but otherwise linear
PET	5.97	5.93	4.38	4.14	4.28	-----	bilinear
PP	4.33	-----	3.91	3.44	-----	-----	bilinear
PTFE	0.9	0.8	1.3	1.7	2.2	3.1	bilinear
PVC	6.05	-----	4.84	4.51	-----	-----	bilinear
PVDF	6.41	-----	6.06	4.47	3.88	-----	bilinear

for not attributing this to experimental error are that the other polymers tested under the same conditions do not show this dip and also that this unexpected observation was checked by repeating the measurements.

Although small specimens were used at strain rates greater than 10^3 s^{-1} in order to minimize radial inertial effects [9, 27, 28], there still remains the possibility that the variety of rate behaviour observed at these high strain rates may be a thickness effect due to differences in plastic wave velocity [29]. We hope in future work to check this possibility by measuring the plastic wave speeds in these materials directly by performing high-speed photography of the deformation of cylinders of these materials fired against rigid targets (the Taylor test: [35, 36]).

One noticeable feature of these experiments is that there is no apparent sign of any effect of the isothermal to adiabatic transition either in the stress/strain graphs (the lines are almost parallel) or in the stress/ln $\dot\varepsilon$ graphs (most show no change of slope at strain rates between 1 and 10 s^{-1}, which is where the transition is expected on simple heat diffusion theory [25, 37, 38]).

Table II. — *Strain rate sensitivity parameter* $(\partial \sigma / \partial \ln \dot{\varepsilon})/$MPa *for* $\dot{\varepsilon} = 10^{-3} - 10^4$ s^{-1}.

Polymer	Max. or flow stress	$\varepsilon = 0.1$	$\varepsilon = 0.2$	$\varepsilon = 0.3$	$\varepsilon = 0.4$	$\varepsilon = 0.5$	Notes
ABS	21	20	17.5	-----	-----	-----	-----
Acetal	-----	-----	-----	-----	13	-----	-----
N66 dry	-0.4	-----	-1.0	-3.0	-3.89	-----	linear drop
PET	16.3	15.2	12.7	12.2	10.6	-----	very linear
PP	11.4	-----	9.1	8.70	-----	-----	-----
PTFE	6.0	5.8	6.0	6.8	8.8	11.8	-----
PVC	16	-----	11	9.8	-----	-----	-----
PVDF	24	-----	31	27	22	-----	-----

Table III. — *Maximum stress/*MPa *supported for various strain rates (actual strain rates can be obtained from the graphs in Fig. 2).*

Polymer	10^{-2}s^{-1}	1s^{-1}	20s^{-1}	2×10^3s^{-1}	6×10^3s^{-1}	2×10^4s^{-1}
ABS	34.2±0.8	42.5±0.5	50±1	61±0.5	96±1.5	109±5
Acetal	73.7±0.8	105±2	110±2	129±1	150±5	159±2
Noryl	81.3±0.3	101±1	114±2	127.7±0.8	114±2.5	120±4
N6 dry	88.6±0.8	114±1	119±2	153±0.5	153±2	157±1
N66 dry	92±1	121±1	133±2	159±1	159±5	158±3
PBT	56.9±0.3	78±2	91±3	110±0.5	107±5	124±4
PC	69.8±0.6	86.5±1	94±4	112±0.5	93±1	108±2
PEEK	100±1	120±3	133±3	153±1.5	122.5±1.5	121±4
PES	79.7±0.9	97±3	107±2	118±2	101±2	113±2
PET	83.6±0.8	103±2	121±3	153±1	174±1.5	193±6
PP	33.6±0.3	53±2	67±3	91±0.5	95±6	113±1
PVC	64±1	84±1	101±3	131±2	159±2	172±4
PVDF	58.7±0.3	87±2	102±3	134±3	157±5	194±12

Note: only those polymers showing a maximum in some of the stress-strain curves are included in this table

The temperature rise we expect for each polymer can be estimated simply as the work done per unit volume (i.e. $\sigma \varepsilon$) divided by the volume heat capacity (i.e. ρC_V, where ρ is the density and C_V is the specific heat capacity). Using figures obtained from a standard data book [39], we estimate the temperature rise for each strain increment of 0.1 to be 7 K for PC, 5 K for acetal, 2.5 K for HDPE and 1.5 K for PTFE. From equation (2), a temperature rise is equivalent to deforming the material at ambient temperature at a lower strain rate according to the following relation:

$$\ln \dot{\varepsilon}_1 = \frac{T_0}{T_0 + \Delta T} \ln \dot{\varepsilon}_0, \tag{6}$$

where T_0 is the ambient temperature (295 K), $\dot{\varepsilon}_0$ is the imposed strain rate, $\dot{\varepsilon}_1$ is the equivalent strain rate. Thus points on the stress/$\ln \dot{\varepsilon}$ graph are shifted to the right of where they should be if there were no temperature change. However, the effect is small: at a strain of 0.2, the factor

Table IV. — *Stress/MPa supported at a strain of 0.2 for various strain rates (actual strain rates can be obtained from the graphs in Fig. 2).*

Polymer	$10^{-2}s^{-1}$	$1s^{-1}$	$20s^{-1}$	$2\times10^3s^{-1}$	$6\times10^3s^{-1}$	$2\times10^4s^{-1}$
ABS	33±1	43±1	-----	61±1.5	88±2.5	101±5
Acetal	71±2	101±1.5	108±4	127±2	150±7	158±2
HDPE	20±1	31.5±1	35±2	41.0±0.5	47±4	48.5±1.5
Noryl	75.7±0.2	91.8±0.3	102±3	113±1	105±4	112±1
N6 dry	84.4±0.7	107±1	117±3	152±1	150±5	155.5±0.6
N6 moist	48.5±0.1	67±3	84±2	114±1	107±7	117.0±0.7
N66 dry	89±2	113.0±0.3	127±5	159±2	156±9	157±2.5
N66 moist	66±2.5	86±1	104±3	134±6	128±5	140±2.5
PBT	55.3±0.6	69±1	77±1	97±1	92±6	106.5±1.5
PC	66.0±0.5	77.5±0.5	87±3	102±1	90±4	108±1
PEEK	99±2	123±3	133±4	148±1	123±1	124±2
PES	78±2	89.5±1.5	96±1	105±2	96±3	108±1
PET	80±2	98±2	113±1	134±2	150±1	167±2
PP	33.0±0.5	54±2	67±1.5	83±1	86±5	101±1
PTFE	10.0±0.5	25±1	23±2	27±1	34±2	41±2.5
PVC	55.3±0.9	73.0±0.3	87±3	110±2.5	125±3	139±1
PVDF	55.0±0.2	85±4	100±2	126±1.5	134±6	171±3

$\dfrac{T_0}{T_0 + \Delta T}$ is 0.95 for PC and 0.99 for PTFE. We conclude that the isothermal to adiabatic transition is unlikely to cause a noticeable change in slope in the stress/ln $\dot{\varepsilon}$ plots at this strain.

Three, however, (acetal, HDPE, PTFE) *do* appear to show a smaller rate sensitivity in the strain rate range $1 - 10^3$ s^{-1} than they do between 10^{-2} s^{-1} and 1 s^{-1}, but without more data points in the low strain rate range, it is not possible to say that this is definitely the case. All the other polymers show a linear relationship between stress and ln $\dot{\varepsilon}$ over the strain rate range $10^{-2} - 10^3$ s^{-1} to a high degree of accuracy (regression coefficients of 0.995 or better). Thus equation (4) can be simplified to

$$V_a = kT \left(\frac{\partial \ln \dot{\varepsilon}}{\partial \sigma} \right)_{P,T}. \tag{7}$$

Activation volumes can therefore be calculated from table I by taking the reciprocal of the figures given and multiplying by 4.07×10^{-21} J (i.e. kT at 295 K). The rate sensitivities given in table I can be seen to vary from 6.33 to 0.8 MPa which translates to activation volumes of $0.64 - 5.1 \times 10^{-21}$ m^3. These are far too large to be accounted for by elementary molecular processes, for an aromatic polymer molecule consisting of 1000 monomer units each of size $5 \times 5 \times 5$ Å has a volume of approximately 10^{-25} m^3. It should be noted that two amorphous polymers (PC and PES) have activation volumes larger than those for some of the semi-crystalline polymers, implying that we cannot necessarily interpret these volumes in terms of crystallites.

The activation volumes for those showing a linear rise in rate sensitivity above 10^3 s^{-1}, although an order of magnitude smaller ($1.3 - 7.0 \times 10^{-22}$ m^3), are still very much greater than the size of individual polymer molecules.

The interpretation of negative slopes for the rate sensitivity in terms of activation volumes is not obvious.

6. Conclusions.

The paper presents the results of a detailed study of the strain rate sensitivity of a wide range of polymers of practical interest. Special efforts have been made to obtain data to high accuracy and at various strain rates. The data should be of direct interest to engineers. However, not all of the features of the curves can be explained at present. We trust this will be stimulus for more experimental work and also analysis by theoreticians.

Specific conclusions and suggestions for future work are:

(i) all but three of the polymers studied (acetal, HDPE, PTFE) showed a linear relationship to a high degree of confidence between compressive stress supported at a given strain and $\ln \dot{\varepsilon}$ over the strain rate range $10^{-2} - 10^3$ s^{-1}. This implies that a simple activated rate theory is adequate to model plastic deformation over this range of strain rates;

(ii) as the rate sensitivity was observed to vary only weakly with strain (with the exception of PTFE and PVDF), it does not matter greatly at which strain the rate sensitivity is calculated for. We recommend that the rate sensitivity of the maximum stress (if the polymer shows a load drop) and the stress supported at a natural strain of 0.2 should be reported;

(iii) ten out of the seventeen polymers studied showed a sudden change of rate sensitivity at a strain rate of around 10^3 s^{-1}. Five of those showing this change showed an increase, but the other five showed a *decrease* in rate sensitivity. The other seven showed no clear change in rate sensitivity over the strain rate range investigated. In addition seven of the twelve polymers that either showed no change or a decrease in rate sensitivity also exhibited a dip in strength around a strain rate of 10^4 s^{-1}. The variety of behaviour observed above 10^3 s^{-1} may be a real material rate effect or alternatively may be due to appreciable differences in the speed of propagation of plastic waves in the various polymers leading to the specimens not being in equilibrium during the tests. In future work, we plan to measure the plastic wave speeds in polymers by means of the Taylor test;

(iv) the activation volumes calculated from the rate sensitivities are very large compared with the volume of individual polymer molecules;

(v) the strain rates that it would be interesting to explore in more detail at room temperature are (a) $1 - 10$ s^{-1} (the transition from isothermal to adiabatic deformation), particularly for those polymers for which there is some evidence for a change of slope in this region (acetal, HDPE, PTFE), (b) 10^3 s^{-1}, where many polymers show a sudden change in rate sensitivity, and (c) 10^4 s^{-1}, for those polymers showing an apparent dip in strength at this strain rate;

(vi) the effect of temperature should be studied so as to obtain the activation enthalpy from the relation $\Delta H_{\mathrm{a}} = kT^2 \left(\dfrac{\partial \ln(\dot{\varepsilon}/\dot{\varepsilon}_0)}{\partial T} \right)_{P,\sigma}$ [15].

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