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Heating effects in the deformation of thermoplastics

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Abstract

The deformation of a plastic material is normally accompanied by a change in temperature, which depends on the character of the process taking place. Low stresses cause small reversible strains with minimal time factors. In this regime there is general compliance with the classical laws of elasticity and the Joule–Thomson equation. Under tension the temperature drops, and in compression it rises. Both these changes can be measured quite accurately, from which the ratio of the coefficient of linear expansion to the specific heat may be derived.

When the applied stresses are increased, large time-dependent deformations take place which are accompanied by an increase in temperature. A method of estimating this temperature change is reviewed, in which the temperature distribution in a tensile test piece under necking conditions is measured using infrared thermovision. The results are shown to follow a semi-empirical double-reciprocal relation between the rise in temperature and the rate of extension, from which an estimate can be made of the proportion of the applied work which is converted into heat. It is concluded that, under the conditions used, most of the applied mechanical energy appears as heat and there is an indication that the measured heat increase may even exceed the predicted level. Possible reasons for this effect are discussed.

Keywords: Deformation; DSC; Hookean; Polymer; Thermoplastic; Thermovision

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1. Introduction

This paper summarises some previous work on the relation between the mechanical and thermal properties of polymers and reviews the results in the light of more recent knowledge.

When a plastic material is deformed, its temperature will change. The amount and the direction of the change depends on the nature and magnitude of the

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deformations which take place and the forces involved. Each component in the deformation process provides a particular type of thermal effect, so that simultaneous thermal and mechanical measurements provide a useful tool for interpreting mechanical behaviour. However thermal changes are not only important as a tool of research. They are also important in themselves because of the way in which the mechanical properties of thermoplastics change with temperature.

Consider the case of a conventional notched impact test. Because of the speed at which the test is carried out, the deformation process will be adiabatic and therefore accompanied by changes in the temperature of the test piece. At the moment of impact, a high tensile strain will be generated at the notch and this causes a slight reduction in temperature, perhaps by 1°C. Later, large deformations will occur, either by massive deformations at the base of the notch, or within the highly localised limits of a craze. In either case the part of the material which is deformed will heat up. Indeed in some cases the rise in temperature may be enough to reach the softening temperature [1,2] as shown in Fig. 1. However, as the temperature of the material is raised towards the softening temperature the stresses required for deformation fall to a low value and the capability of the material to absorb energy is reduced. This means that there is an upper limit to the energy ($W_{\max}$) which a given volume of thermoplastic can absorb, i.e.

$$W_{\max} = \rho V C_p (T_S - T_0)$$

where ρ is the density, V the volume of material affected, C_p the specific heat at constant pressure (in this case the average over the relevant temperature range), and T_S and T_0 are the softening and ambient temperatures respectively.

In this review, two types of temperature response will be considered. Firstly those connected with the initial Hookean elasticity and, secondly, those which occur during large deformation processes and necking. The Hookean elasticity is that which occurs at low stresses and strains, and generally follows the classical laws of elasticity. Thus the strain generated by any particular stress field may be determined by any two of the four elastic constants, e.g. Young's modulus E and Poisson's ratio μ. Within a relatively wide range of stresses the deformation and thermal effects occur immediately and both are reversed when the stress is removed. An account of the experimental measurement of this type of temperature effect will now be given.

2. The thermoelastic effect at low strains

The changes in temperature which occur when an elastic solid is subjected to a stress are predicted by the Joule–Thomson equation [3] which may be formulated as follows

$$\Delta T = \alpha T \Delta\sigma / \rho C_p \tag{1}$$

where α is the coefficient of linear expansion, ρ the density, and ΔT and $\Delta\sigma$ are the increments of temperature and stress (negative for tension) respectively. This

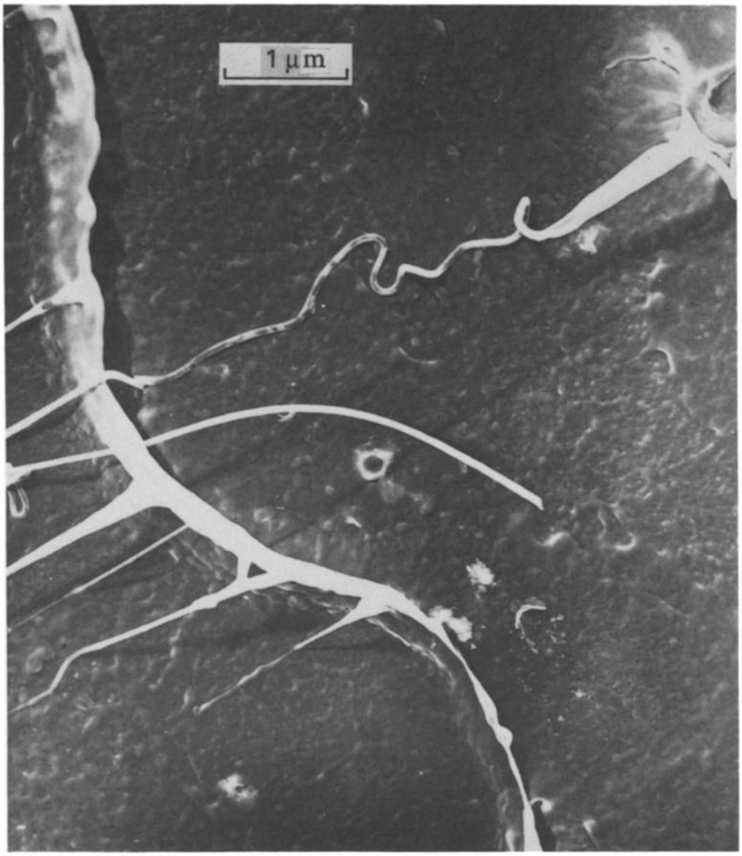

Fig. 1. Electron microscopic picture of fracture surface obtained when a small bar of polystyrene is broken at room temperature. Craze material is formed and extended adiabatically to give melted strands (Ref. [1], Fig. 7b). Reproduced with permission from *Polymer*.

equation has been verified for metals and other materials but has not been extensively studied with plastics, although the large values of the expansion coefficients would predict significant changes in ΔT. With plastics the first observations were reported by McNally and Shepherd [4] with cellulose ester film; later the work of Binder and Müller [5] demonstrated reversible changes in temperature in response of fluctuations in applied stress.

The subject has been quantitatively studied for several glassy polymers in two papers [5,6]. Experiments were carried out both in tension and compression, but in tension it was found that the process of moulding a thermocouple in the test piece weakened it excessively so that it became necessary to employ the less satisfactory procedure of sandwiching the sensor between two strips of plastic. With compression tests this difficulty did not arise and the first experiments soon showed that measurements of ΔT were able to provide an encouraging level of reproducibility.

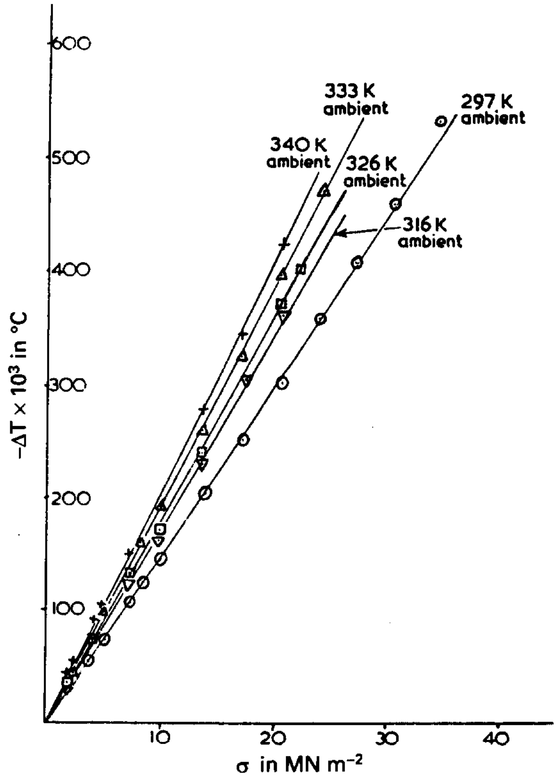

Fig. 2. The change in temperature with applied tensile stress for PMMA at different starting temperatures (Ref. [6], Fig. 4).

Even the measurements in tension showed a good linearity between the change in temperature and the applied stress (Fig. 2) [6].

The programme of work was then carried out using compression tests. Cylinders were moulded from two discs pressed together so as to encapsulate a fine chromel–alumel thermocouple. For this purpose, a split-chase mould was used which was well lagged so as to provide a uniform moulding temperature. It was also found necessary to polish the faces of the test piece so as to ensure completely flat surfaces. Under these conditions a recorder output of the type shown in Fig. 3 was obtained. Several other variables which might have affected the results were also investigated in this research, including the use of lubricants, annealing procedures and the aspect ratio of the test pieces. Of these factors only the aspect ratio was found to be important, probably due to a barrelling effect under stress. Aspect ratios above 1.5 were found to be necessary and were always used in the later work. The differences between the results in the first paper [6] and those obtained later [7] are believed to be due to the use of low aspect ratios in the first paper.

According to Eq. (1), the observed temperature change ΔT should be proportional to the stress increment $\Delta\sigma$ and the absolute temperature T. Both these

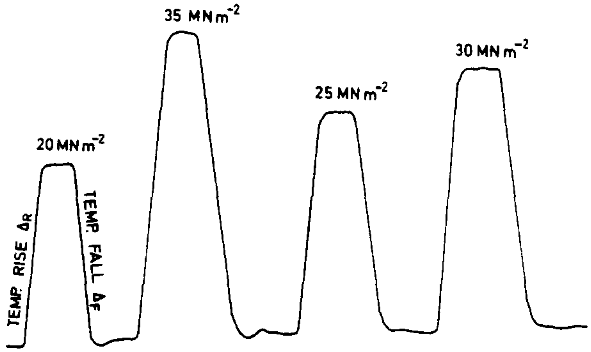

Fig. 3. The temperature changes following the application and removal of a compressive stress with polystyrene. Typical recorder output from experiment (Ref. [7], Fig. 1).

predictions were readily demonstrated as shown in Figs. 4 and 5, where good straight lines are shown. These suggested that it would be possible to make measurements with a good degree of accuracy. The materials used in this study were polystyrene (PS), poly(methyl methacrylate) (PMMA), polycarbonate (PC) and an araldite epoxy resin.

From Eq. (1), it will be seen that measurements of the reversible thermoelastic effect readily provide a value of the quantity α/C_p. In order to derive either of these separately one of them has to be measured directly. In the work of Gilmour et al. [7], the specific heat was measured by differential scanning calorimetry (DSC) and the values obtained were compared with literature values (Fig. 6). The two sets of measurements could then be combined to give values for α, the linear expansion coefficient. Results for the four materials studied will now be discussed. Details of the particular types of material used are given in Ref. [7].

2.1. Polystyrene

A relatively pure, heat resistant grade of polystyrene (HR) was used in the work [7] which had a rather high glass transition temperature of 373 K as determined by DSC. A few comparisons were also made with a general purpose moulding grade (GP) containing an internal lubricant with a T_g of 362 K. When measured at the same temperature the HR material gave a slightly smaller thermoelastic signal than the GP polymer, but when the materials were compared in terms of T/T_g, the differences disappeared. Because most commercial polystyrenes are nearer to the GP grade than to the HR, some discrepancies may be due to this factor. For example, it can be seen in Fig. 6A that the relatively small variation in specific heats between the different results could be accommodated by a temperature shift of some 10 K.

Once C_p and the density had been determined, the value of α could be calculated from the thermoelastic effect according to Eq. (1), as shown in Fig. 7. Here the results obtained fell among the other published results at room temperature and above, but at lower temperatures there were increasing differences when compared with the measurements reported by Roe [13].

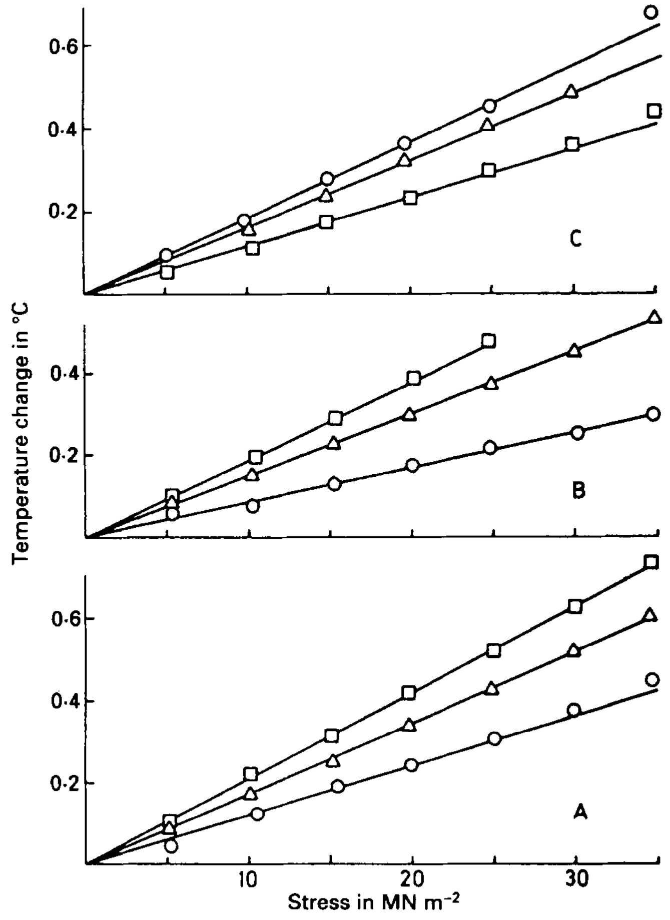

Fig. 4. Thermoelastic temperature changes as a function of stress. A, polystyrene HR: ○, 222 K; △, 298 K; □, 333 K. B, PMMA: symbols as for PS. C, polycarbonate: □, 222 K; △, 303 K; ○, 358 K (Ref. [7], Fig. 6).

2.2. *Poly(methyl methacrylate)*

With this polymer the specific heat measurements agree well with the earlier work [6] and also with the results of Wunderlich and Bauer [11]. Somewhat different figures were reported by Melia [10] especially at higher temperatures. All the results for α are in good agreement (Fig. 7).

2.3. *Epoxy resins*

The DSC measurements of specific heat were in line with those of Wunderlich and Bauer [11] but it was found that the thermoelastic effect differed appreciably

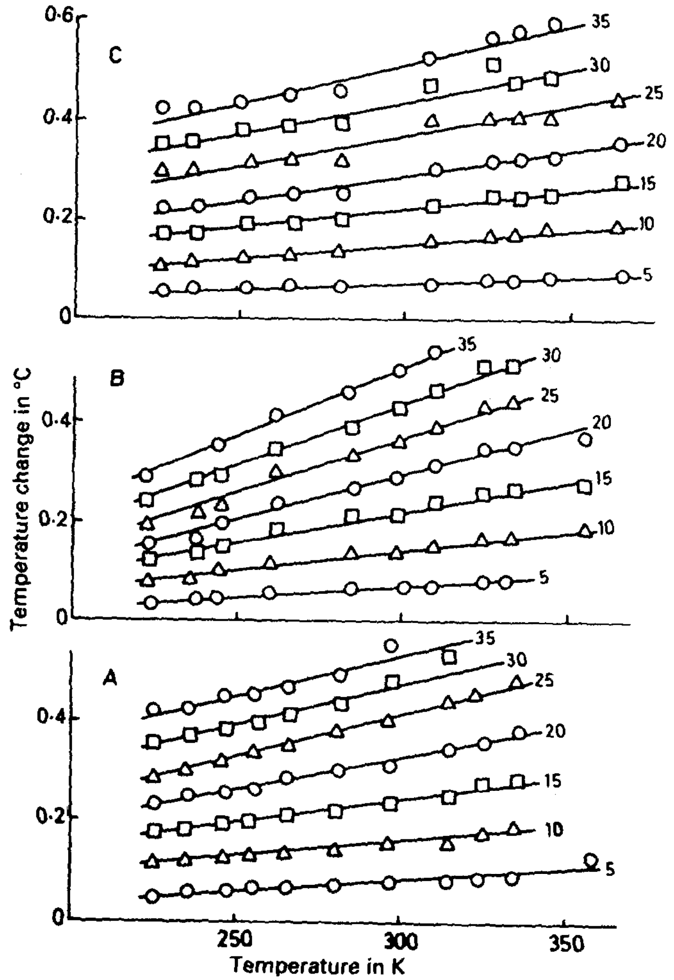

Fig. 5. Thermoelastic temperature change as a function of ambient temperature. A; PS; B; PMMA; C, PC. The numbers indicate the applied stress in MN m^{-2} (Ref. [7], Fig. 7).

for different samples of the resin, leading to different values of the expansion coefficient (Fig. 7D). The normal linear dependence of ΔT with stress and temperature was observed in all cases.

2.4. Polycarbonate

With this plastic, Gilmour's results agree well with those of Adam [12] (measured earlier in the same laboratory) and the expansion coefficients are similar to the independent results recorded by Roe (Ref. [13], Fig. 7C).

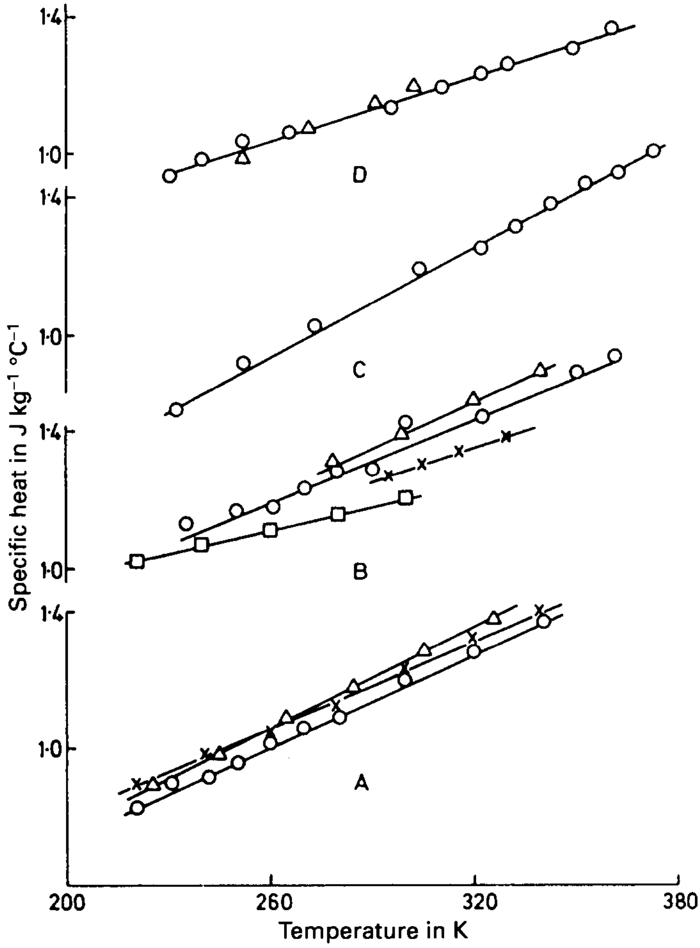

Fig. 6. Specific heat against temperature. A; Polystyrene HR: ○, Ref. [7]; △, Ref. [8]; ×, Ref. [9]. B, PMMA: ×, Ref. [6]; □, Ref. [10]; ○, Ref. [7]; △, Ref. [11]. C, araldite resin: ○, Ref. [7]. D, PC: ○, Ref. [7]; △, Ref. [12]. (Figure from Fig. 5, Ref. [6].)

3. Determination of the Gruneisen coefficient

Gruneisen first put forward the concept of a constant relating thermal and mechanical properties of materials in his theory of the solid state [19] and this has become known as the Gruneisen constant γ where

$$\gamma = V(\mathrm{d}P/\mathrm{d}U)_V$$

Later Warfield [20] discussed the application of Gruneisen's theory to plastics and proposed some modifications to his proposals. He argued that for plastics it was necessary to distinguish between two models for the vibrations of a polymer

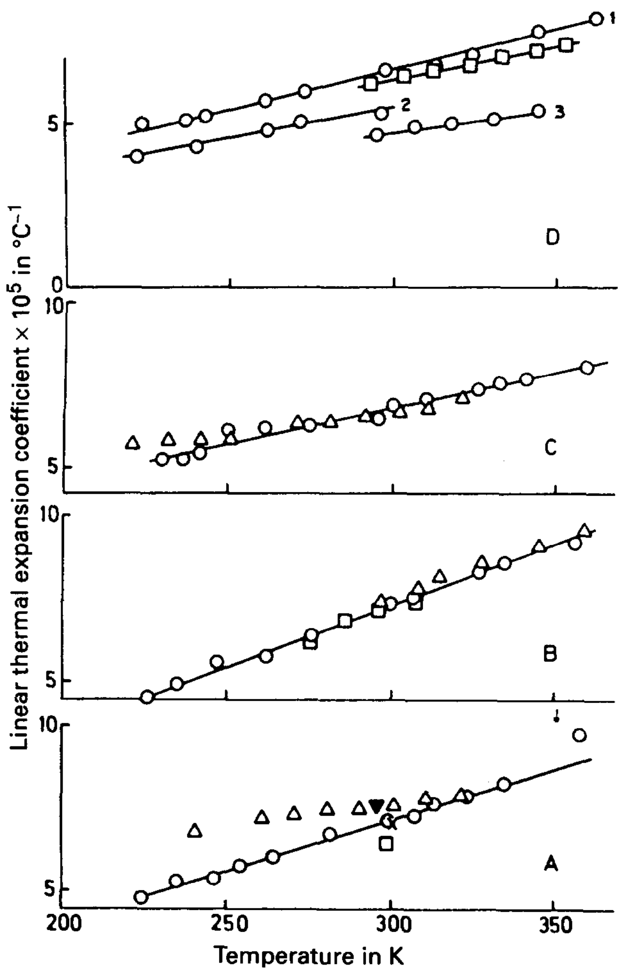

Fig. 7. Linear thermal expansion coefficient as a function of temperature. A, polystyrene HR: ○, Ref. [7]; △, Ref. [13]; ×, Ref. [14]; □, Ref. [15]; ▲, Ref. [16]. B, PMMA: ○, Ref. [7]; △, Ref. [17]; □, ICI Ref. [6]. C, polycarbonate: ○, Ref. [7]; △, Ref. [13]. D, araldite resin: ○, Ref. [7]; □, Ref. [18]. Numbers 1–3 refer to different resin preparations. (Figure from Ref. [7], Fig. 9).

chain, namely vibrations that affect interactions between chains (low frequency, long wavelength, external degrees of freedom) and true intrachain vibrations (high frequency, short wavelengths) which do not affect interchain contacts. These distinctions lead directly to the hypothesis of two Gruneisen constants for plastics, one derived from interchain vibrations called the lattice constant γ_L, and another which is calculated from parameters such as specific heat, dependent on all vibrational modes, called the thermodynamic Gruneisen constant γ_T. This constant γ_T contains the quantity $\alpha V/C_V$ which, after applying a small correction to the value of C_p [21], is directly determined by the thermoelastic effect. Such measurements should therefore lead directly to an improvement in the accuracy of determination of γ_T which is useful because previous measurement of γ_T show a much wider variation than those for γ_L [20]. The results obtained in this way give a value of 0.52 for polystyrene and 0.47 for PMMA [22]. Both results fall within the rather wide scatter of previous measurements and also show a reduced variation with temperature.

4. Thermal methods for the study of large deformations

4.1. Qualitative studies

In the previous section an account has been given of the manner in which small temperature changes may be used to study low strain thermoelastic effects in thermoplastics. In this work it was found that measurements in tension were more difficult to carry out than measurements in compression, because even the smallest thermocouple probe became a source of weakness. When large deformations are studied these problems are increased, expecially when it is desired to measure heating in a moving neck at high extension ratios (λ), where λ is given by (extended length/original length.)

It was therefore decided to investigate the possibility of employing a commercial infrared camera (AGA Thermovision 680) to observe the temperature changes in a test piece during the necking process. Some initial exploratory experiments which served to demonstarate the general capability of the equipment were carried out as illustrated in Figs. 8A and B [23]. These first results demonstrated a striking effect which had not previously been reported. When a tensile test piece is extended in a necking mode the active neck where drawing is taking place may be situated at either of both ends of the already drawn central part of the test piece. In the absence of any heating effect it would have been expected that both ends would be active since this would reduce the relevant strain rate and hence the drawing stress. Under the conditions used this is what happened with polycarbonate, but with rigid PVC only one neck was active (Fig. 8B, below). It was concluded that under the conditions used the greater temperature sensitivity of the PVC lead to a reduced drawing stress when all the energy input was located in a single neck. This proposal is in line with the material properties listed in Table 1.

4.2. Thermal fracture

When yielding takes place in a conventional tensile test piece using PVC the deformation process is initiated in a shear band which provides enough deformation so that the stress can drop to the level required for stable necking. However if the stress is prevented from falling then the rate of strain will increase and become adiabatic, leading to a thermal fracture. With PVC, this may be accomplished simply by lengthening the test piece [24]. Under these conditions the temperature in the shear band rises from 298 to 320° K (Fig. 9), which is high enough for a

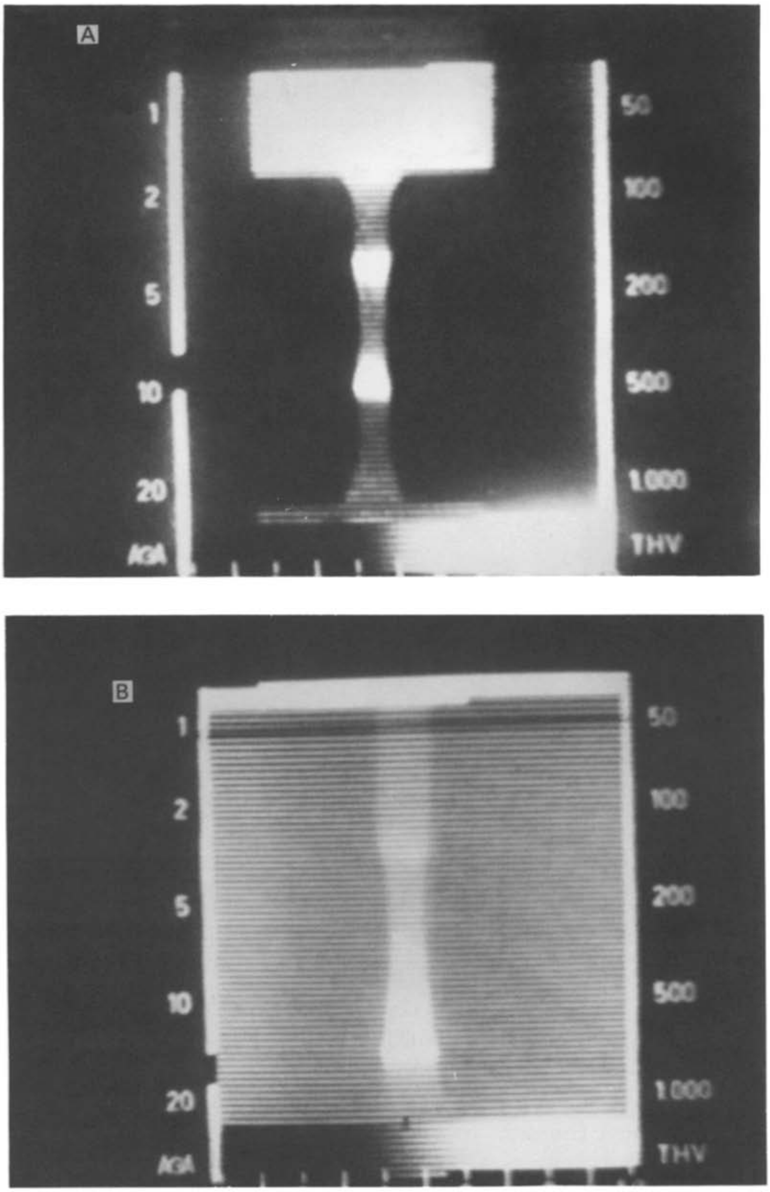

Fig. 8. Thermovision picture of the necking process in two thermoplastics (Ref. [23], Figs. 1 and 2). A, polycarbonate; B, PVC. In these pictures the brighest parts of the test piece correspond to the highest temperatures.

ductile fracture to propagate through the shear band with some local melting. With polycarbonate, the same lengthening effect can only be observed after the material has been annealed to increase the yield stress and so augment the stored elastic energy [24].

Table 1
Temperature and strain rate sensitivity of PVC and polycarbonate plastics

	Polycarbonate	PVC
Temperature sensitivity $d\sigma/dT/(\mathrm{MN\ m^{-2}\ K^{-1}})$	−0.25	0.71
Strain rate sensitivity $d\sigma/d\ln\lambda/\mathrm{MN\ m^{-2}}$	1.0	1.5
Glass transition temperature/K	433	340

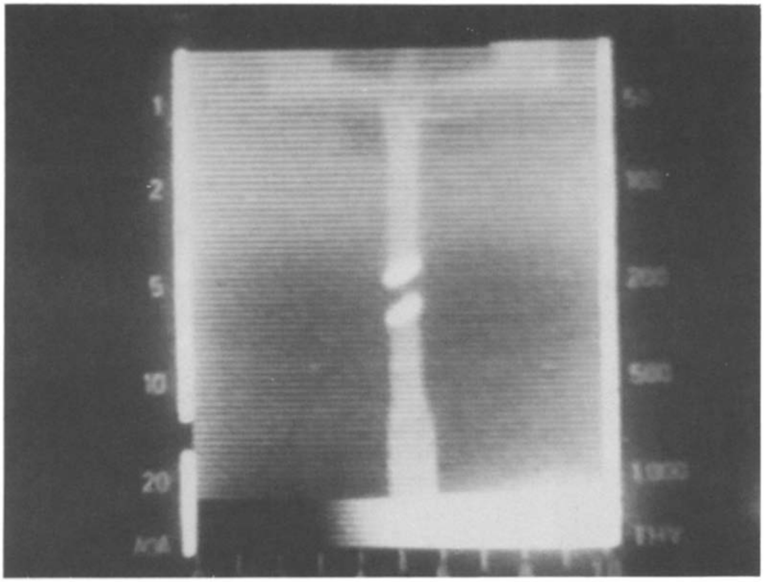

Fig. 9. Thermovision picture of the thermal fracture of PVC.

There is some evidence that similar thermal processes can play a part in the fracture of other materials. For example, Marsh [25] has proposed that glass breaks through a localised flow process at stresses of 3–8000 MN m^{-2} depending on the time of the experiment (minutes to microseconds.) Any fast adiabatic deformation at such stresses would cause large rises in temperature and a consequent emission of light. In a separate study of the impact fracture of glass beads, Weichert and Schonert [26] measured the radiation emitted. By recording its intensity at four preselected wavelengths they were able to estimate momentary local temperatures of about 3200 K which were shown to be generated in a layer 2 nm thick at the point of fracture. Thus in spite of the huge local energy absorption, the volume in which this occurred was so small in relation to the mass of the material employed that the fracture was seen to be brittle. This process has obvious analogies with the fast fracture of a plastic craze in which melting can also be observed (Fig. 1), and with the shear banding and fracture of steel at high rates of loading as observed by Giovanola [27].

5. Quantitative measurements

5.1. Use of thermovision to measure temperature

In order to measure the temperature distribution on a plastic test specimen during the necking process, a coloured photograph is taken which is represented in

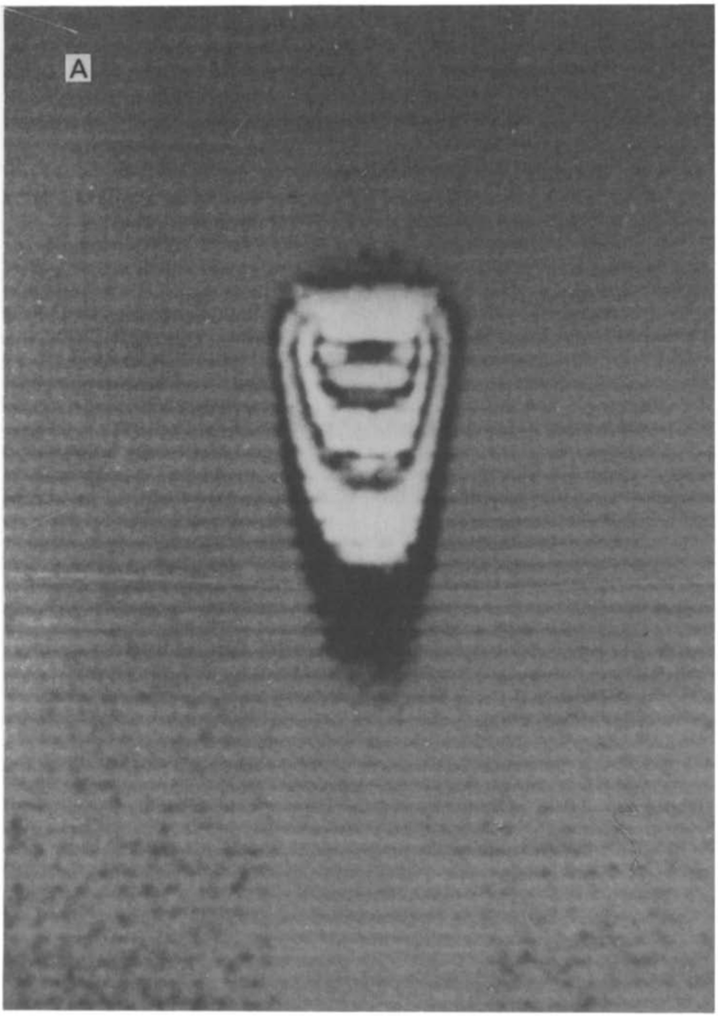

Fig. 10. A, thermovision picture illustrating the temperature distribution during the necking of polycarbonate.

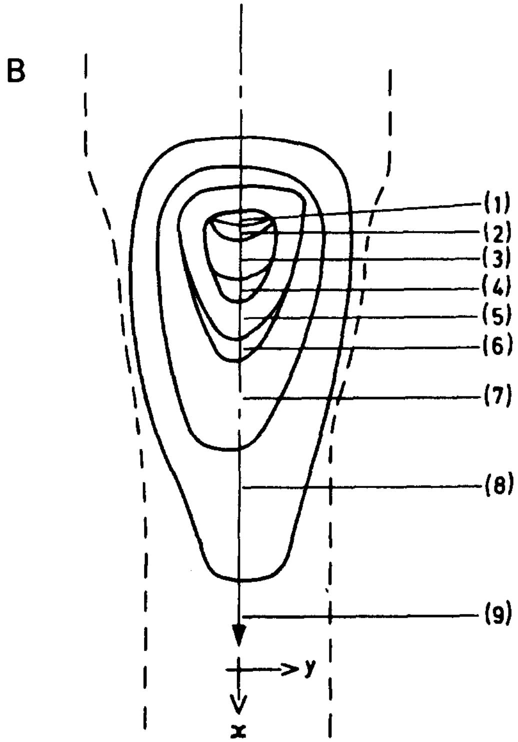

Fig. 10. B, diagram of the temperature profile of a necking polycarbonate specimen: (1) 39.3°C; (2) 37.3°C; (3) 35.3°C; (4) 33.5°C; (5) 31.5°C; (6) 29.9°C; (7) 27.7°C; (8) 25.6°C; (9) 23.0°C. (Ref. [28], Figs. 1a and b.)

monochrome in Fig. 10 [28]. Taking the picture combines a number of operations which exploit the capabilities of the equipment. At a preselected temperature, any area of a thermal picture can be made to show bright white with the rest of the picture dark. The isotherm so presented can be programmed to scan the test piece and thus mark out the temperature variation on the surface. A coloured picture representing the different temperatures can then be built up in the following way. A polaroid camara is attached to the front of the screen and the thermovision isotherm is set to jump through a series of positions in time with a sequence of colour filters so that each colour corresponds with a particular temperature. This then gives a picture of the type shown in Fig. 10A from which the temperatures shown in Fig. 10B can be read off. To ensure that the thermovision reading related correctly to the temperature of the specimen and to eliminate background radiation, black test pieces were used (except in one case with polycarbonate). These were shown to be opaque to radiation from an IR lamp. Emissivity was checked by comparing thermovision readings with temperature measurements made using thermocouples embedded in the surface of black plastic sheets. These could be heated by an IR lamp at an angle from behind.

5.2. Sample preparation of testing

The failure of a plastic test piece during necking process can be unpredictable because the post-yield fracture process is initiated from small defects in the material [29]. With the black plastics used, this problem may have been accentuated by occasional aggregates of carbon black. Details of the methods and materials used are given in Ref. [28]. Generally, the plastic was remoulded by pressing into sheets and in the case of polycarbonate the hot polymer was quenched in cold water to reduce annealing effects and consequent brittleness [30,31]. This increased the tendency to give premature fracture especially at high rates of extension. Before testing, the samples were flexed at one end of the test piece to initiate necking which was then in a position to progress in one direction along its parallel length. This gave the necking process a chance to stabilise and to propagate at a constant rate. The temperature distribution could then be recorded at a series of different extension rates which were provided by a conventional Instron tensometer.

6. Results and discussion

In this treatment we omit the small thermoelastic effect and relate the heating effect to the mechanical work and heat losses during the necking process. Thus

Mechanical work done on the test piece

= Measurable heat retained by specimen

+ heat lost to atmosphere

− changes in internal energy ΔU

Then, neglecting internal energy effects at this stage, we can usefully simplify the presentation by defining two quantities

α_M = Measurable heat/mechanical work

and

α_T = (Measurable heat + heat lost to atmosphere)/mechanical work

To estimate these quantities from the experimental results the following relations (2)–(7) are used

$$\text{Mechanical work} = Lgv_C t_n \tag{2}$$

where L is the constant necking force in kg, $g = 9.81\ \mathrm{N\ K\ g^{-1}}$, (both together give the force in N) v_C is the drawing speed, and t_n is the time of the necking process.

In order to calculate the measurable heat generated in the test piece it is necessary to know the volume of necked material. This was measured by substracting the length of the specimen which had not necked from the original length and multiplying by the original width and thickness. Each part of this volume was then considered to have been heated to the temperature of the "hot spot" following the centre line in Fig. 10B, so that

$$\text{Measurable heat} = V\rho C_p(T_S - T_0) \tag{3}$$

where V is the volume of necked material, ρ the density, C_p the specific heat, and T_S and T_0 the steady state temperature of the hot spot and the ambient temperature respectively (K).

In the experimental studies on the thermal effects of necking the main variable employed was the speed of extension (v_C) which is obviously related to the heat loss. As v_C is increased, heat losses will be reduced and at the limit of "infinite rate" will become zero. This trend is illustrated in Fig. 11A and B where the results for α_M are plotted against the reciprocal of drawing speed for four plastics, polycarbonate (PC), poly(vinyl chloride) (PVC), polyethylene (PE) and polypropylene (PP). It can be seen that, except in the case of PVC where experimental problems were encountered with premature fracture at high speeds, the value of α_M rises towards unity at high rates of extension.

It has further been found that the thermal changes may be usefully analysed by making the simplifying assumption that heat losses are proportional to the temperature difference between the test piece and its surroundings and by replacing the actual temperature profile shown in Fig. 12A by that shown in 12B, where the hot spot has been squared off to an area A such that the rate of heat lost from it at a temperature T_S is equal to that from the whole deformation region. Then

$$\text{Heat loss} = kA(T_S - T_0)t_n \tag{4}$$

where k is the rate of heat loss per K at ambient temperature. We can then write

$$\alpha_T g v_C t_n = kA(T_S - T_0)t_n + V\rho C_p(T_S - T_0) \tag{5}$$

Because the values of $v_C t_n$ and V both depend on the total length of the experiment they can be eliminated by using the equation

$$V = abv_C t_n(D - 1) \tag{6}$$

where a, b are the original length and thickness of the specimen, and D is the draw ratio (length of neck/original length). Then substituting Eq. (6) into Eq. (5) and putting $(T_S - T_0) = \Delta T$, we get

$$\frac{1}{\Delta T} = \frac{kA}{Lg\alpha_H v_C} + \frac{ab\rho C_p}{(D-1)Lg\alpha_H} \tag{7}$$

A similar equation may be derived from the more complex analysis of fluctuating drawing stresses by Barenblatt [32]. When the drawing stress is constant, as in the present experiments, then, using his notation $d\sigma_1/dt = 0$ and $V = v$. The heat balance equation then becomes

$$\begin{aligned}\text{Total heat liberated} &= Q\omega V\\ &= \text{Heat loss} + \text{heat retained by sample}\\ &= B(T - T_0)S\,dt + cVS_2(T - T_0)\,dT\end{aligned}$$

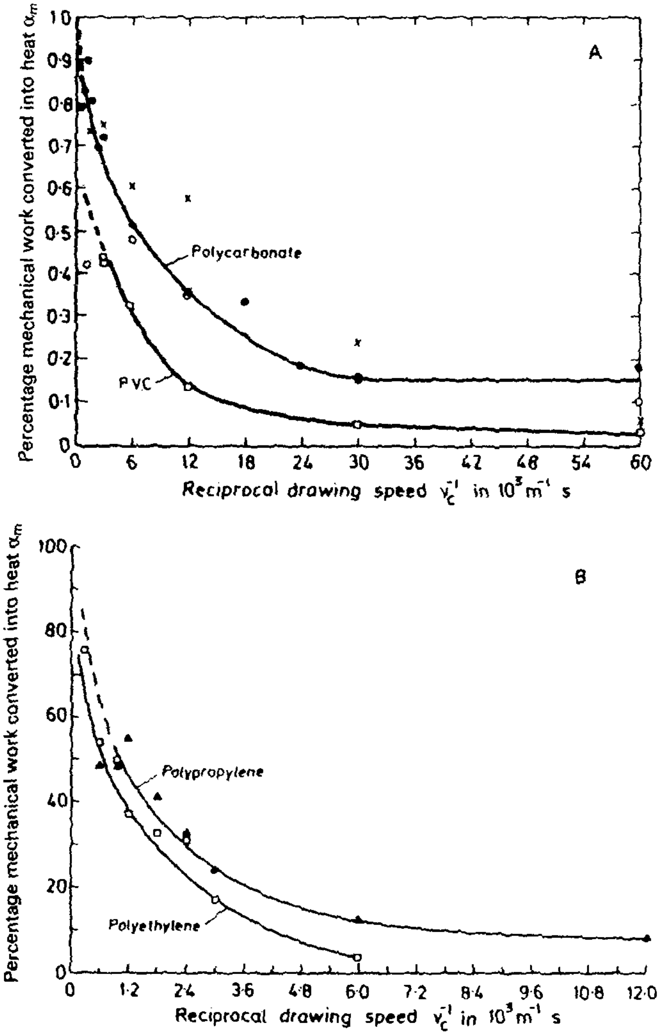

Fig. 11. The conversion of mechanical energy into measurable heat during necking. A, polycarbonate and PVC sheet: ×, PC black quenched; ●, PC clear; ○, PVC black quenched; □, PVC clear. B, other plastics as shown. The curves show the proportion α_M of the applied work converted into the measurable heating of the specimen as a function of drawing speed. (Ref. [28], Fig. 3.)

Then, putting $(T - T_0) = \Delta T$, we get

$$1/V(BS/Q\omega) \simeq CS_2/Q\omega$$

which leads to an equation of the same form as Eq. (7).

Under the conditions used in experiments to evaluate Eq. (7), it was found that both D and L were sensibly constant and changed little with the rate of extension, i.e. as far as L was concerned the increase of temperature in the neck approximately compensated for the normal increase in yield stress with strain rate. Further, in

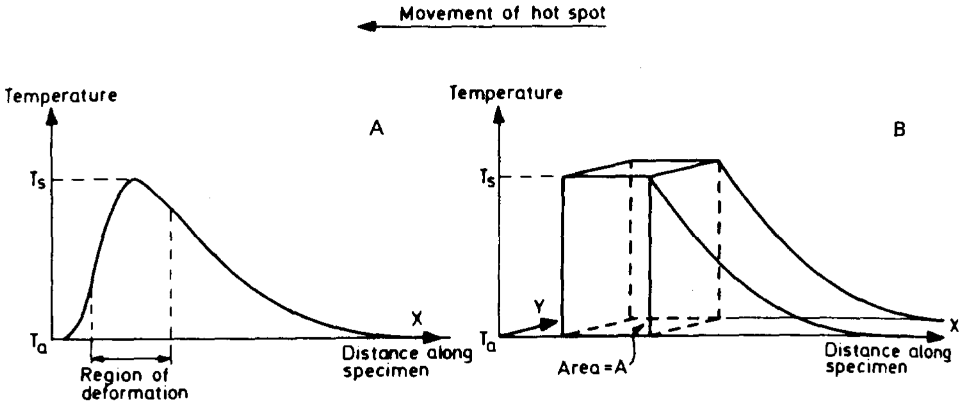

Fig. 12. Simplified treatment of the temperature profile necking (Ref. [28], Fig. 12).

Table 2
Estimated value of α for conversion of mechanical work to heat

Material	α	Standard error [a]
Quenched polycarbonate	1.06	±0.03
High-density polythene	1.15	±0.39
Polypropylene	1.03	±0.11
Poly(vinyl chloride)	Errors too great for useful estimate	

[a] Errors from other sources will bring the total errors for polycarbonate and polypropylene up to about ±15%. It will be appreciated that the extrapolation of the reciprocal plots allows the determination of α_H at a very high speed, essentially independent of the deviation of equation (7).

practice it was found that plots of $1/\Delta T$ against $1/v_C$ were remarkably linear as shown in Fig. 13A and B. The extrapolated values of ΔT at "infinite speed" eliminate the unknown factor k and so enable values of α_T to be calculated as shown in Table 2. It will be seen that the extrapolated temperature rises are quite considerable, ranging from about 30 K for polycarbonate to 70–80 K for the polyolefins with their much higher draw ratios.

It will be seen that in each case α_T values greater than unity are reported. In view of the uncertainty and novelty of the method, it cannot be confidently asserted that this is actually the case. However the results provide an incentive to consider the various types of thermal response which might be associated with large strains in tension.

7. The thermal effects of large strains in tension

According to the present author, true stress–strain curves in most thermoplastics in tension may be quantitatively described by a model including three

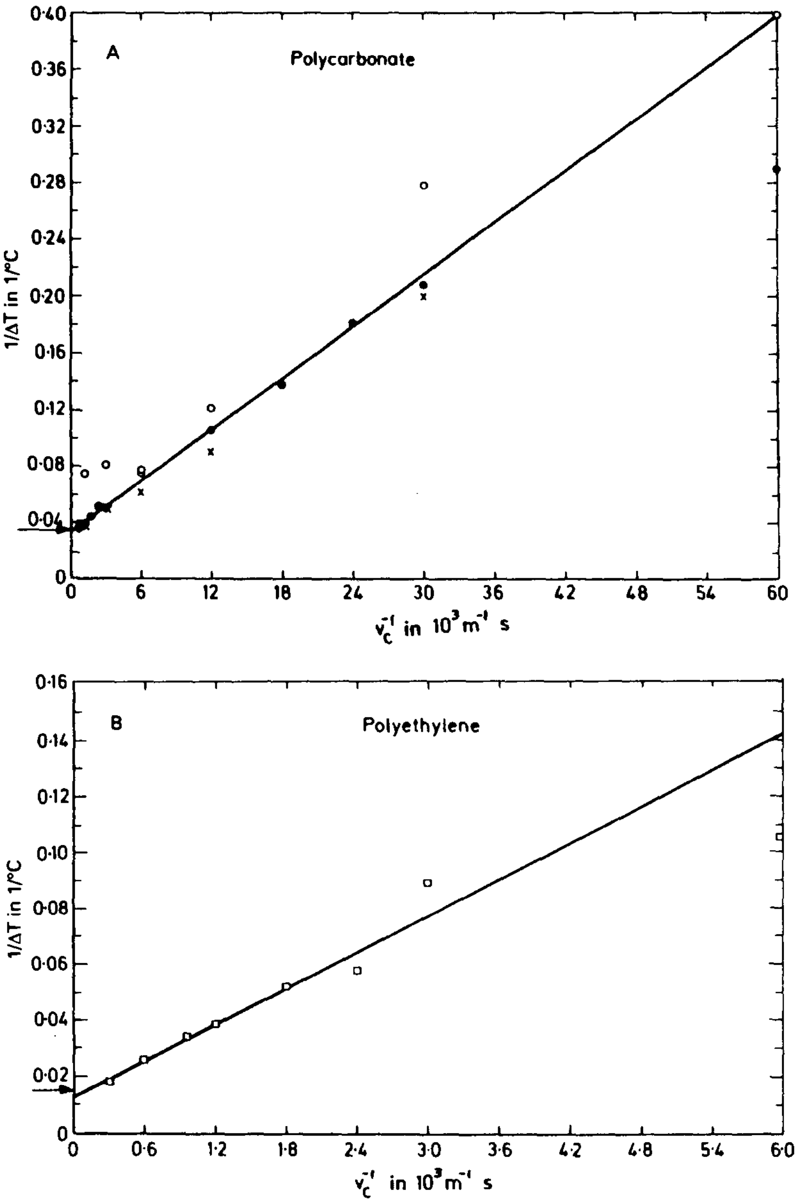

Fig. 13. Linear reciprocal plots showing temperature rise against drawing speed for: A, polycarbonate and B, polyethylene. (Ref. [28], Fig. 5.)

elements [33–35]: an initial Hookean elasticity; frictional viscosity; and entropic effects due to the exhaustion of available chain conformations as in rubber elasticity [36].

The thermal consequences of such a model are quite clear. The Hookean elasticity will cause a small initial drop in the temperature of the test piece. Then, during the large deformation process there will be a rise in temperature directly related to the mechanical work. The factors which can cause a deviation from the predictions of the model will now be discussed.

7.1. Hookean elasticity

Although the thermal effects of this type of deformation are quite clear, there are still some ambiguities concerning the manner in which it can affect the measurable heat generated by a large strain. For example in the case of a tensile test there is normally an increase in the true stress as the experiment continues. Thus the initial selection and subtraction of an observed Hookean strain may not apply correctly in the later stages of the test.

7.2. Physical ageing

Glassy polymers do not provide a true equilibrium state as a starting point for any particular experiment. In particular the thermal history of the material after cooling below T_G can affect the value of the internal energy, as may be measured by differential scanning calorimetry (DSC). For example when a polymer which has been aged at a temperature just below T_G is deformed under tension, the initial yield stress may be raised significantly and this provides additional energy to make good the deficit which developed during the ageing process [30,31]. However the extent to which this mechanical work is converted into heat is not known. Neither has the mechanism of the physical ageing process been clearly established though a reduction in free volume [37] and a change in the distribution of rotational isomers has been proposed [38,39].

7.3. Plastic shear defects

Recently Oleinik [40,41] has studied the heating effects in glassy polymers under compression. In the first part of the deformation process, i.e. at compressions of 20%–40%, an additional energy sink has been found which could reduce the value of α_T in this strain range to a figure as low as 0.5. It is proposed that in the early stages of deformation, plastic shear defects are generated which store energy and constitute an essential preliminary to the plastic deformation process. It is possible that this effect is greater in compression than in tension because of the larger stresses involved.

7.4. Changes in crystallinity

Many polymers undergo changes in crystallinity during a deformation process. For example poly(ethylene terephthalate) (PET) starts to crystallise at an extension ratio of about 2.5 in a tensile test [42], and Meinel and Peterlin [43] have recorded an increase in crystallinity for polethylene at high strains, though the overall change depended critically on the starting density which was not measured in the experiments described here. Nevertheless it is clear that any such changes could have a significant thermal effect. For example, with a heat of fusion of 8 kJ mol^{-1} and a specific heat of 1.9 kJ kg^{-1} K^{-1} [44], an increase of 5% in crystallinity would lead to a temperature rise of 7–8 K with a consequent rise in α_T. This effect is readily measured with natural rubber which crystallises at high strains [36,45].

7.5. Changes in rotational isomers

This subject has already been mentioned in connection with physical ageing, where, however, the evidence is still somewhat meagre. With large deformations this is not so. Increases in the trans configuration for polystyrene extended above T_G have been reported by Stolting and Müller [46], with reductions in U of up to 4 kJ kg^{-1}. Similar changes have been observed with PET [42,47], and at the beginning of the deformation process with styrene polymers [48]. More recently, computer simulation studies with a polyethylene-like material have indicated an increase in the proportion of the trans isomer of about 5% with an extension ratio of 2. As the energy difference between the two isomers is variously estimated as between 2.3 and 4.4 kJ per mol of C–C bonds [49–51], the effect of such changes can only be roughly estimated. This applies particularly to normal polyethylenes where the gauche form exists only in the amorphous phase at a concentration of 10%–25% [50,52], which inevitably limits further reductions at higher strains. Taking a crystallinity of 60%, a 5% reduction in gauche isomers and an average energy difference of 3 kJ mol^{-1}, the rise in temperature would be about 2 K. At the higher strains characteristic of the necking process, the temperature increase might be significantly higher.

8. Conclusions

The measurement of temperature changes during small Hookean deformations makes it possible to estimate the quantity α/C_p with a good degree of accuracy.

The application of infrared thermovision to the study of the necking and fracture of thermoplastics yields novel and interesting results. A start has been made with the quantitative investigation of thermal effects during necking. There is a good reciprocal relationship between the maximum temperature rise and the rate of extension. The results point to the possibility that the observed heating of the test piece can exceed that due to the applied mechanical work, though with a new and previously untried technique the differences may not have been significant.

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