The Effect of Strain Rate on the Stress–Strain Curve of Oriented Polymers.   II.   The Influence of Heat Developed During Extension

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Synopsis

The temperature changes which take place in a yarn during extension are considered. From thermodynamical considerations and the heat-transfer coefficient it is shown that extension of the yarns studied will take place isothermally at strain rates below 0.04 sec.$^{-1}$ and adiabatically at rates above 4 sec.$^{-1}$.   It is not possible to make an accurate estimate of the magnitude of the temperature rise during adiabatic extension, because of the lack of information on internal energy changes during irreversible extension, but by assuming these to be zero it is estimated that the temperature is likely to rise by 20–30°C. at strains above 10%.   Results from a study of the effect of strain rate on the stress–strain curves of five different yarns show in all these materials a range of strain rate in which the stress that produces a given strain increases less rapidly with strain rate than elsewhere.   For viscose and poly(ethylene terephthalate) this effect occurs in the expected range of strain rate, and its magnitude is of the correct order for it to be attributed to the temperature rise resulting from the transition from isothermal to adiabatic extension.   For the other materials the transition does not seem likely to provide a complete explanation of this effect.   There is no evidence that the transition significantly affects the breaking properties.

INTRODUCTION

When a test piece is extended, some of the work done in producing the deformation will appear as heat.   At low rates of deformation this heat will be lost to the atmosphere, and extension will take place isothermally. At high rates of deformation the heat will be generated too quickly to be lost. Extension will therefore take place adiabatically, and the temperature of the test piece will increase as extension proceeds.   This temperature rise would be expected to alter the form of the stress–strain curve and, possibly, the breaking properties.

Various phenomena have been attributed to this heating[1-3] and attempts made to estimate its magnitude.[1,4]   None of these, however, set out the thermodynamics of the process fully, and none makes accurate estimates of the range of strain rates in which the effects occur.

In the present paper this range will be determined by considering the heat generated in and lost from a uniform cylinder of the same dimensions, heat-transfer coefficient, and mechanical properties as the fiber, during

extension at a constant rate. The magnitude of the temperature rise will be estimated by assuming the internal energy changes during extension to be zero. The experimental data presented in Part I[5] of this series will then be studied to see whether any of the changes in the mechanical properties with increasing strain rate can be attributed to these temperature changes.

TEMPERATURE CHANGES DURING EXTENSION

Range of Strain Rate for Temperature Changes

Consider a homogeneous, cylindrical fiber of length L cm. During an interval of time dt sec. let this undergo an extension of dL cm. at a tension of F dynes and simultaneously receive a quantity of heat of dQ cal. from the surroundings. If it is assumed that the volume of the filament is unchanged during this operation, i.e., that $p\ dV$ is negligible, where p is atmospheric pressure, it follows from the first law of thermodynamics that

$$dU = dQ + (F\ dL \times 10^{-7})/4.18 \qquad (1)$$

where dU is the change in internal energy of the fiber in calories.

It is possible to express dU in terms of the fiber's thermal capacity C and its temperature rise dT. This is done by writing

$$dU = (\partial U/\partial L)_{TV}\ dL + (\partial U/\partial T)_{LV}dT \qquad (2)$$

If the thermal capacity of the fiber at constant volume and length is C_{VL} cal./°C., then

$$(\partial U/\partial T)_{LV} = C_{VL} \qquad (3)$$

and substituting from eq. (2) and (3) in (1) gives

$$(\partial U/\partial L)_{TV}\ dL + C_{VL}\ dT = dQ + (F\ dL \times 10^{-7})/4.18 \qquad (4)$$

If the surroundings are at a temperature T_0 °C., which is less than T, then dQ will be negative and will represent the heat lost from the filament during the extension. If it is assumed that Newton's law of cooling is applicable to the conditions of the experiment and that the temperature is uniform throughout the filament, then dQ will be given by

$$dQ = -2\pi rLh(T - T_0)dt \qquad (5)$$

where r is the radius of the filament in centimeters and h the heat-transfer coefficient in calories per square centimeter per degree centigrade per second.

Substituting from eq. (5) in (4) gives

$$[(F + 10^{-7})/4.18 - (\partial U/\partial L)_{TV}]\ dL - C_{VL}\ dT -$$
$$2\pi rLh(T - T_0)dt = 0 \quad (6)$$

Equation (6) is an expression for the rise in temperature, dT, of the filament, which occurs during an extension dL at a tension F in time dt. Before dT

can be calculated, it is necessary to express the other quantities in this equation in the units in which they are measured experimentally.

With textile materials stresses are usually expressed in the units of force (in gram-weight) per unit linear density in the unstrained state, where the unit of linear density is the tex (the weight in grams of 10^5 cm. of filament). If f is the stress in grams per tex and ρ_L the linear density of the filament in tex, then

$$F = 981 f \rho_L \tag{7}$$

It is convenient to use the specific heat and internal energy per unit mass (c_{VL} and u) rather than the thermal capacity and internal energy of the entire specimen of length L.   Now,

$$U = u \pi r^2 L \rho \tag{8}$$

$$C_{VL} = c_{VL} \pi r^2 L \rho \tag{9}$$

where ρ is the density of the material of the filament in grams per square centimeter.

Changes in length dL are usually measured as changes in strain $d\epsilon$, where

$$dL = L\, d\epsilon \tag{10}$$

The radius of a fine filament is not easily determined experimentally, but it can be expressed in terms of the density of the material ρ and the linear density of the filament ρ_L, which are easily measured by the equation

$$r^2 = \rho_L / \pi \rho \times 10^5 \tag{11}$$

Substituting from eqs. (7)–(11) in (6) and writing T' for $(T - T_0)$ and $\dot\epsilon$ for the strain rate $d\epsilon/dt$ gives

$$c_{VL}(dT'/d\epsilon) = 2.35f - (\partial u/\partial \epsilon)_{TV} - 2 \times 10^2 (10\pi/\rho \rho_L)^{1/2}(hT'/\dot\epsilon) \tag{12}$$

This is a differential equation expressing the rate of increase of filament temperature with strain in terms of the rate of straining, filament stress and temperature, and other filament parameters.   It has been derived by using a homogeneous, cylindrical filament as a model.   It may, however, be applied to a multifilament yarn, if it is assumed that the boundary surface of this yarn is cylindrical and that the mean density of the yarn within this surface is ρ.

On the basis of these assumptions Arthur and Jones[6] have given value of $\rho = 1$ (approximately) and $h = 3.2 \times 10^{-3}$ cal. cm.$^{-2}$-°C.$^{-1}$-sec.$^{-1}$ for nylon yarn similar to that used in the experiments to be considered, except that it was highly twisted.   In the ensuing calculation it is assumed that these values have similar magnitudes for all the yarns used in these experiments.

Values of c_{VL} are not given in the literature, but 0.35 cal. g.$^{-1}$-°C.$^{-1}$ is typical for c_p for all polymeric materials, and so this value is used for c_{VL}. Making these substitutions in eq. (12) gives

$$0.35(dT'/d\epsilon) = 2.35f - (\partial u/\partial \epsilon)_{TV} - 3.58T'/\dot\epsilon \rho_L^{1/2} \tag{13}$$

If $(\partial u/\partial \epsilon)_{TV}$ is regarded as a function of the strain and $\dot{\epsilon}$ is constant, then this differential equation, which is of a standard form,

$$dT'/d\epsilon = \phi(\epsilon) - AT'$$

where A is a constant and ϕ represents some function, has the solution

$$T_1' = (1/0.35) \int_0^{\epsilon_1} [2.35f - (\partial u/\partial \epsilon)_{TV}]$$

$$\exp - [(10/\dot{\epsilon}\rho_L^{1/2})(\epsilon_1 - \epsilon)]d\epsilon \quad (14)$$

Here T_1' is the temperature excess at strain ϵ_1 of the filament over its surroundings.

The transition from isothermal to adiabatic extension is described by the exponential term in eq. (14). If $\dot{\epsilon}$ is sufficiently small, this term will equal zero over most of the range of integration, in which case T'_1 will be equal to zero and extension will be isothermal. For sufficiently large values of $\dot{\epsilon}$ the exponential term will be equal to unity over the entire range of integration, and the temperature rise will be given by

$$T_1' = (1/0.35) \int_0^{\epsilon_1} [2.35f - (\partial u/\partial \epsilon)_{TV}]d\epsilon \quad (15)$$

Under these conditions extension will take place adiabatically.

By numerical evaluation of the exponential term it can be shown that most of its change in value from zero to unity occurs for values of $10/\dot{\epsilon}\rho_L^{1/2}$ between 1 and 50 (at strains relevant to the present application). Applying this criterion to the yarns used in the experiments to be considered the transition from isothermal to adiabatic extension would be expected to occur in the range of strain rate shown in Table I.

TABLE I
Transition from Isothermal to Adiabatic Extension

Material	Range of strain rate
Viscose	4×10^{-2} to 2 sec.$^{-1}$
Nylon	7×10^{-2} to 4 sec.$^{-1}$
PET	6×10^{-2} to 3 sec.$^{-1}$
PAN	6×10^{-2} to 3 sec.$^{-1}$
PP	7×10^{-2} to 4 sec.$^{-1}$

Specifications of the materials used are given in Table I of Part I.[5]

Magnitude of Temperature Changes

Besides estimating the range of strain rate in which extension changes from isothermal to adiabatic it is desirable to estimate the magnitude of the temperature change during adiabatic extension. By referring to eq. (15) this will be seen to depend on the $(\partial u/\partial \epsilon)_{TV}$ term.

For an ideal rubberlike material extended under reversible condition this term is, by definition, zero. All the mechanical work done in extend-
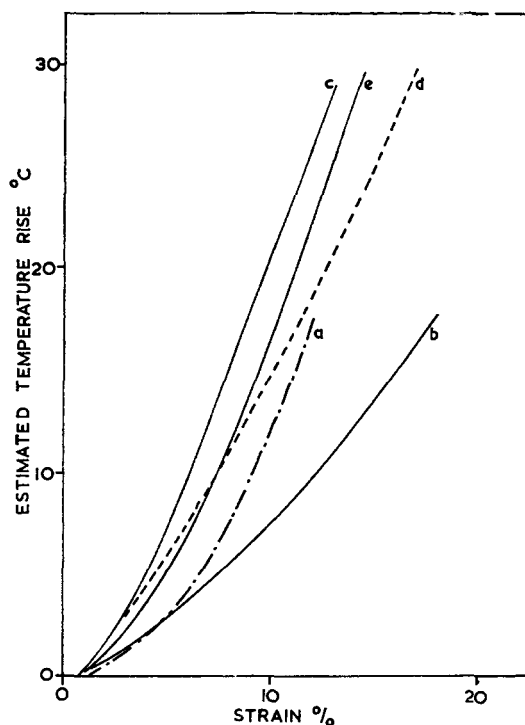
Fig. 1. Estimated temperature rise during extension: (a) nylon; (b) viscose; (c) PET; (d) PAN; (e) PP.

ing such a material would appear as heat.   Many amorphous rubbers closely approach this in behavior but it is unlikely that semicrystalline rubbers and glasses do so.   Quantitative experimental data is, however, very unsatisfactory on this point.

Dart[7] has measured $(\partial u/\partial \epsilon)_{TV}$ for a number of fibers under thermodynamically reversible conditions and has shown it to be of a magnitude comparable to f, though slightly smaller.   In the experiments to be considered, however, extension is not reversible in the thermodynamic sense, as shown by the rate dependence of the stress.   The time scale of the experiments is also very different from that of Dart's.   Both these factors might be expected to influence the value of $(\partial u/\partial \epsilon)_{TV}$, and so it would be unreliable to use Dart's values in the present calculation.

Müller has studied the heat evolved during the extension of polymers (this work is reviewed by Ke[8]).   For unoriented, semicrystalline polymers this is often negative at small extensions but becomes positive with orientation.   It would therefore most likely be positive for textile fibers.   The experiments, however, are not quantitative and so are of little value in the present application.

Because of these uncertainties only an estimation of one order of magnitude of the temperature rise is possible.   In these circumstances it was

decided to make the simplest possible assumption, i.e., that $(\partial u/\partial \epsilon)_{TV}$ can be neglected compared with f. The temperature rise during adiabatic extension can then be calculated from eq. (15) by integrating the experimental stress–strain curve obtained at strain rates at which extension was adiabatic. This has been done for each of the materials studied experimentally, the stress–strain curve being at a strain rate in the region of 8 –10 sec.$^{-1}$; the results are given in Figure 1. Because the shape of the stress–strain curve varies with strain rate, the precise value calculated will depend upon which stress–strain curve is selected from those obtained at different strain rates in the adiabatic region, higher strain rates leading to greater rises. However, this effect is likely to be small compared with the uncertainties inherent in the calculation so far.

The assumption that internal energy changes can be neglected implies that all the work done appears as heat. This is unlikely in partially crystalline materials, and so the estimates of temperature rise are probably overestimates. However, if there were changes in crystallization during extension, this would not necessarily be true. An increase in crystallinity would liberate heat, causing temperature rises above those calculated.

The main conclusions of the preceding argument may be summarized as follows: the transition from isothermal to adiabatic extension will occur within the two decades of strain rate from 0.04 to 4 sec.$^{-1}$, and the temperature rise during adiabatic extension will be of the order indicated in Figure 1.

EFFECT OF TEMPERATURE CHANGES ON TENSILE PROPERTIES

Form of Stress–Strain Curve

For a discussion of the effect of the transition from isothermal to adiabatic extension upon the form of the stress–strain curve information on the sensitivity of the stress–strain curve to temperature is necessary. This is likely to depend on the strain, strain rate, and temperature, besides the material, an sufficiently detailed information is not available for a complete discuss 1. Therefore, for some data as a guide to the discussion, stress–strain urves were determined at temperatures of 0 and 35°C. at a strain rate in the isothermal–adiabatic transition region for PP and PAN. These indicated that with PP a 10°C. rise in temperature would cause a 5% decrease in the stress to produce a given strain, whereas with PAN it would produce a 10% decrease. It will be assumed that the temperature sensitivity of the other three materials is the mean of these two values.

In the subsequent discussion the curves of stress that produces a given strain (which are obtained from the experimental data presented in Part I)[5] will first be considered, and changes occurring in the range of strain rate from 0.04 to 4 sec.$^{-1}$ that might be attributable to the transition from isothermal to adiabatic extension will be identified. The data of Figure 1 and the above-given estimate of sensitivity to temperature changes will then be used for determining whether the changes in mechanical behavior are of right order of magnitude to be attributed to thermal effects.
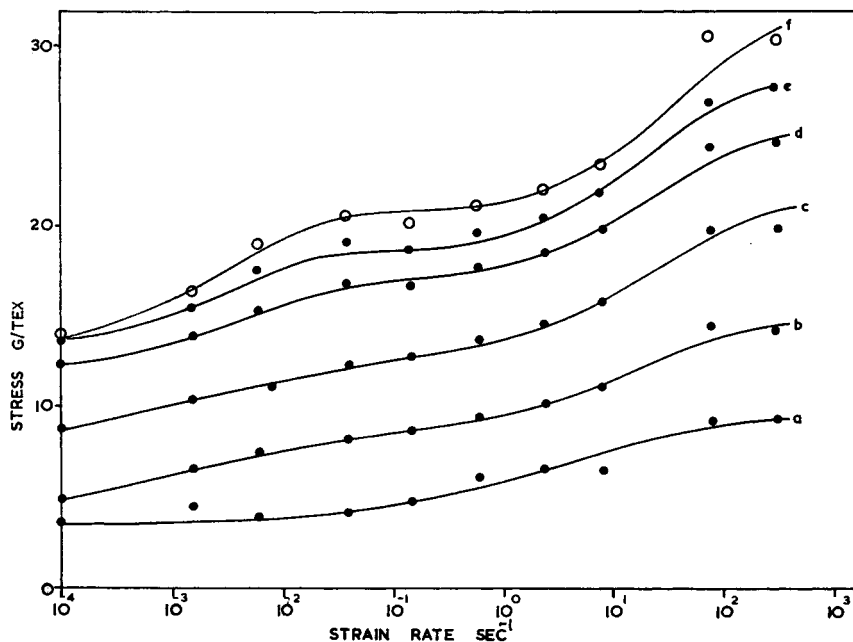
Fig. 2. Effect of strain rate on the stress needed to produce strains in viscose (%):
(a) 1; (b) 3; (c) 10; (d) 15; (e) 18; (f) breaking strain.

From Figures 2–6 it will be seen that for each material the rate of increase stress with strain rate is lower in the two decades 0.04 to 4 sec.$^{-1}$ (called a plateau) than at any other rates, which might be a consequence of thermal changes. However, with nylon this effect does not commence until rates considerably higher than 0.04 sec.$^{-1}$ (particularly at low strains) and persists to rates higher than 4 sec.$^{-1}$.

TABLE II

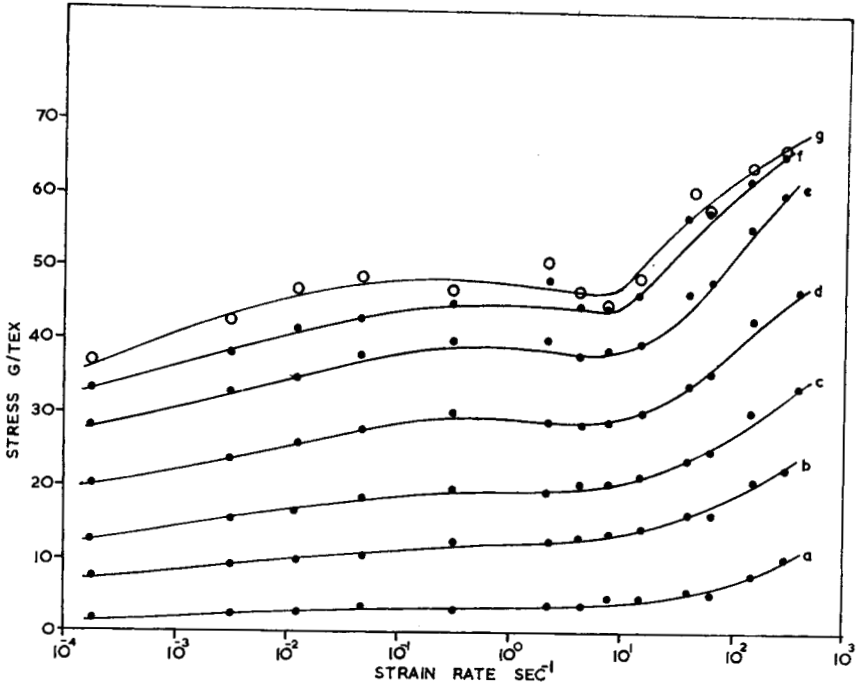| Material	Strain, %	Estimated temperature rise, °C.	
		Required to produce observed changes	Produced by adiabatic extension
Viscose	18	12	18
	3	2	1
Nylon	12	32	18
	6	24	4
PET	12	10	25
	4	2	4
PAN	17	6	30
	6	3	8
PP	15	24	32
	5	34	7

Fig. 3. Effect of strain rate on stress needed to produce strains in nylon (%): (a) 1; (b) 4; (c) 6; (d) 8; (e) 10; (f) 12; (g) breaking strain.
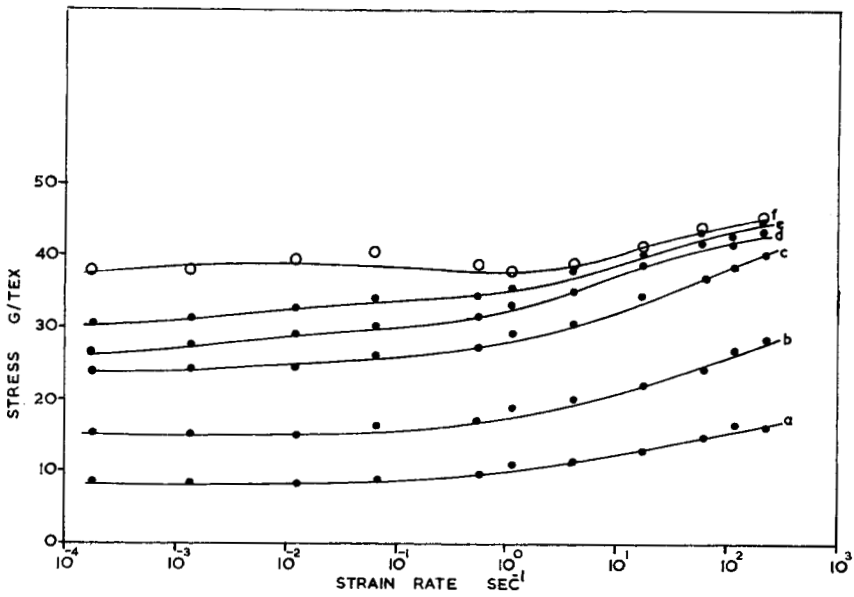

Fig. 4. Effect of strain rate on stress needed to produce strains in PET (%): (a) 1; (b) 2; (c) 4; (d) 6; (e) 12; (f) breaking strain.
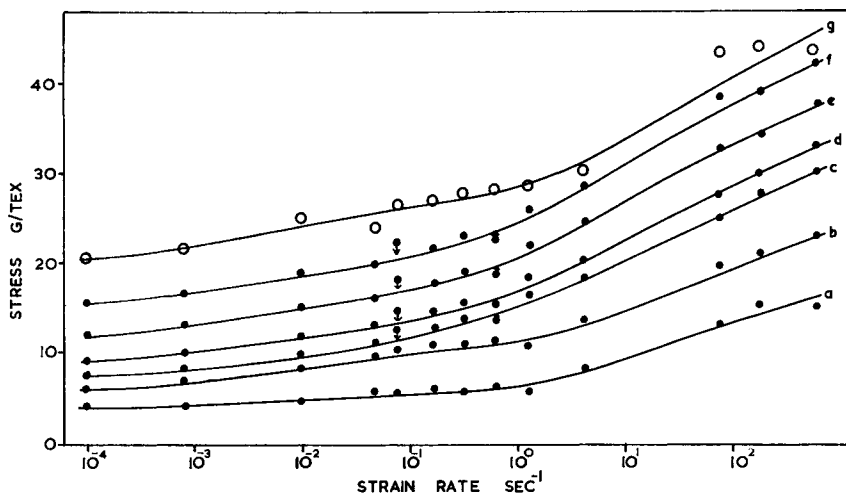
Fig. 5. Effect of strain rate on stress needed to produce strains in PAN (%); (a) 1; (b) 2; (c) 6; (d) 10; (e) 14; (f) 17; (g) breaking strain.
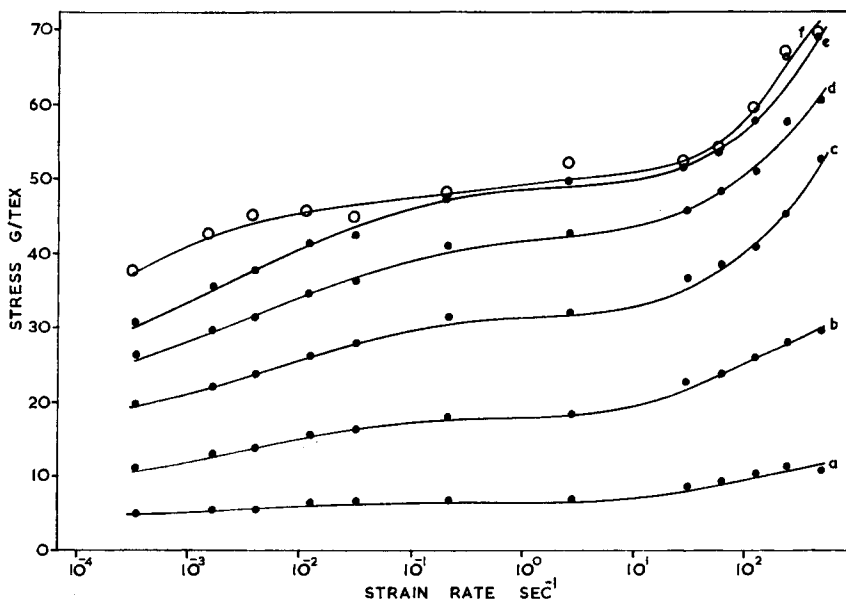

Fig. 6. Effect of strain rate on stress needed to produce strains in PP (%): (a) 1; (b) 4; (c) 8; (d) 12; (e) 17; (f) breaking strain.

To determine whether the changes were of the right order of magnitude to be attributable to thermal effects the curves in the region of 0.04 sec.$^{-1}$ were smoothly extrapolated to a rate of 4 sec.$^{-1}$. It was then assumed that the difference in stress between the extrapolated and observed value was due to thermal effects, and the temperature rise necessary to produce

this difference was estimated from the temperature sensitivities given above. In Table II this temperature rise is compared with that which would be expected to be produced by adiabatic extension (from the data of Fig. 1).

From Table II it will be seen that, if the uncertainties in the values of these temperature rises are taken into account, then for viscose and PET the two sets of values are not significantly different. It would therefore seem likely that for these two materials the plateaus in Figures 2 and 4 are caused by the transition from isothermal to adiabatic extension. If nylon and PP are now considered, then for the former material at both strains shown in Table II and for the latter at the small strain a much larger temperature rise would be required to produce the observed effects than is likely to be produced by adiabatic extension; thus, for these two materials the plateaus shown in Figures 3 and 6 are unlikely to be accounted for solely by thermal changes. This conclusion is confirmed by the range of values of the strain rates over which these plateaus occur. With nylon this range occurs at higher strain rates, and with PP it is wider than would be expected if the plateaus were caused soley by thermal effects.

If PAN is now considered it will be seen from Table II that the temperature rise required to produce the effects observed in Figure 5 is much smaller than might be expected to be produced by adiabatic heating. However, this would not be unreasonable, if there were a significant change in internal energy during extension.

An indication of whether or not temperature rises are affecting the mechanical properties measured in these experiments is obtained by a different means when methods of viscoelastic analysis of the present results are considered.[9] This indicates the likelihood of temperature changes in all materials except PP and PAN, which supports the conclusions concerning PET, viscose, and PAN. It also suggests that thermal effects, do not contribute at all to the plateaus observed with PP, which is substantially in agreement with the conclusion that they are not its sole cause.

Thus it may be concluded that the plateaus observed with viscose and PET are caused by the transition from isothermal to adiabatic extension but that those observed with PP and PAN have some other cause. The plateau observed with nylon is unlikely to be caused solely by thermal effects, though these might contribute.

The plateaus discussed above reflect variations in the shape of the stress–strain curve with strain rate. These variations should be detectable in the families of stress–strain curves at different rates, given in Part I.[5] There are two particular examples of this, the first with PET and the second with nylon, that should be noted. Both of these examples are thought to arise from the same cause; that the heat developed during adiabatic extension would be expected to cause the slopes of the stress–strain curve to be less at strain rates in the adiabatic region than in the isothermal. From Figure 1 this effect should be most noticeable at large strains. Thus with PET the slope of the stress–strain curve beyond the yield point should

be lower at rates above 1.2 sec.$^{-1}$ than below 1.3 $\times$ 10^{-2} sec.$^{-1}$. This might lead to the intersecting of the curves at these particular rates, which is observed in Figure 3 of Part I.[5] The intersection of the curves at rates of 3.2 $\times$ 10^{-1} and 4.9 $\times$ 10^{-2} for nylon (Fig. 2 of part I[5]) would probably have a similar cause.

EFFECT OF TEMPERATURE CHANGES ON BREAKING PROPERTIES

It is possible that a change in temperature will affect the breaking properties of the fiber.   Indeed, Vincent[3] has argued, without giving direct evidence, that at strains above the yield strain an increase in temperature with increasing extension will lead to instability in the test piece, precipitating fracture and so causing the strain at break to fall sharply with increasing strain rate in the range in which the change from isothermal to adiabatic extension occurs.   It has been shown already[10] that this theory does not provide an adequate explanation of the change with strain rate in the breaking strain of P.P.   Similarly, from Figure 6 of part I[5] it will be seen that only in the case of nylon is there a sharp fall in breaking extension occurring in a range of strain rate, such that it might be caused by thermal effects. However, since for four other polymers temperature changes have been shown not to influence the breaking extension, the possibility that this will happen with nylon must be considered unlikely, until more evidence is available.

CONCLUSIONS

From thermodynamical considerations and the heat-transfer coefficients of the yarns it has been estimated that for filaments of normal radial dimensions extension will change from isothermal to adiabatic in a range of strain rate from 0.04 to 4 sec.$^{-1}$ Because of a lack of information on internal energy changes during irreversible extension it is not possible to calculate the magnitude of the temperature rise during adiabatic extension, but by assuming these changes to be zero it is estimated that the temperature is likely to rise by 20–30°C. at strains above 10%.

In the curve of stress producing a given strain versus strain rate there is a region in which the slope is less than elsewhere.   For two of the materials (viscose and PET) this occurs in the correct range of strain rate and is of the right order of magnitude to be attributed to the isothermal–adiabatic transition. With the other materials this transition does not seem likely to provide a complete explanation of the observed plateau.   There is no evidence that this transition significantly affects the breaking properties.

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