JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 2825–2832 (1970)

Thermal Runaway of Nylon 6–10 During Drawing Under Constant Load

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Synopsis

Anhydrous nylon 6–10 filaments were cold drawn (by propagation of a preexisting neck) under constant load. The extension rate $\dot{l}$, which is proportional to the neck velocity, was observed to be a continuous function of the load up to a certain critical extension rate $\dot{l}_c$ above which $\dot{l}$ increased discontinuously ("runaway") by approximately two orders of magnitude. If the filament is in N_2 gas, $\dot{l}_c \simeq 0.4$ cm/min, whereas if it is in He gas, $\dot{l}_c \simeq 1$ cm/min. The structure of the drawn filament produced by runaway is an opaque, microvoid structure which, after a suitable change in load, forms first in the center of a filament and spreads toward the surface. This instability is attributed to the heating of the shoulder of the neck during neck motion. An analysis based on the meaured activation enthalpy for neck motion and the thermal properties of nylon and the gas is used to predict $\dot{l}_c$ values that are in rough agreement with experiment.

INTRODUCTION

The role of heating in neck formation and propagation during cold drawing of a polymer has been a point of controversy. It was originally suggested that the formation of a neck was basically due to the formation of a localized hot spot at a point in the specimen (inhomogeneous) where the plastic strain rate was highest[1] and that the temperature at the shoulder of the propagating neck was raised above the glass transition temperature.[2,3] This concept has been shown to be not sufficiently general, particularly because cold drawing still takes place at such low elongation rates in some polymers that the deformation is essentially isothermal.[4,5] The thermal initiation hypothesis has given way to the idea that neck formation will occur according to Considère's construction,[5] that is, when the polymer either actually strain softens or does not strain harden enough to prevent the geometric instability. On this basis, heating is only one possible mechanism of strain softening; in fact, most experimental evidence,[6,7] including direct measurements of the temperature of the forming neck,[8] indicates that the temperature rise during the early stages of neck formation (initial yield) is negligible.

On the other hand, it is also widely known that heating at the shoulder can markedly affect the stress needed to propagate the neck in the conventional constant elongation rate test and that such propagation stresses

must be interpreted with caution. It has not been recognized, however, that heating will produce an inherent instability in the neck propagation rate in a creep, or constant load, test. This instability, which is referred to here as thermal runaway because it is analogous to the thermal runaway of a transitor at constant voltage, is observed to result in a drawn fiber with entirely different properties than that produced by stable neck motion.

EXPERIMENTAL RESULTS

Anhydrous nylon 6–10 monofilaments were drawn under constant load in a dry gas atmosphere in an environmental chamber the temperature of which was held constant to 0.1°C. A detailed account of the preparation and characterization of the nylon, as well as of the mechanical testing apparatus and procedure, has been published elsewhere.[9]

At low steady-state neck propagation velocities, this velocity v_n is both stress activated and thermally activated, that is, v_n obeys an equation of the form[9]

$$v_n = v_0 \exp\{-[\Delta H^* - (V^*\sigma/4)]/k_B T\} \quad (1)$$

where v_0 is a constant, k_B is the Boltzmann constant, σ is the tensile stress in the unoriented fiber, V^* is a shear activation volume, and ΔH^* is an activation enthalpy. It is also useful to define an effective activation enthalpy ΔH^*_{eff} as

$$\Delta H^*_{eff} \equiv \Delta H^* - (V^*\sigma/4) \quad (2)$$

This effective activation enthalpy characterizes the changes in neck velocity due to temperature at constant stress. For these nylon 6–10 samples, ΔH^*_{eff} has been determined previously to be 3.7 ± 0.3 eV.[9]

However, eq. (1) does not hold for high neck velocities. Instead, there is a critical neck velocity above which the neck velocity jumps discontinuously to a value at least two orders of magnitude higher. An example of this behavior is shown in Figure 1, where the logarithm of the steady-state elongation rate is plotted against the stress at constant ambient temperature. (The elongation rate, or velocity of the load, $\dot{l}$ equals v_n(R-1) where R is the draw ratio.) A similar instability occurs if the stress is held constant and the ambient temperature is increased. It is possible to demonstrate, by selecting a sample of nylon (not completely dried) with a lower drawing stress at a given neck velocity, that the criterion for the onset of the instability is that a critical neck velocity (or, more accurately, a critical value of $v_n\sigma$) and not a critical stress or temperature be reached.

The fact that a critical neck velocity, and thus a critical power dissipation, is necessary to produce the instability suggests that it is due to heating at the deforming shoulder of the neck. Very strong support for this idea is provided by the results displayed in Figure 1 of an experiment in which the critical elongation rate for instability was determined in both a nitrogen gas and a helium gas atmosphere. The critical drawing speed $\dot{l}_c$ in N_2 gas is

~0.4 cm/min, whereas in He gas, which has a much higher thermal conductivity, $\dot{l}_c$ is ~1 cm/min. This behavior is what one would expect if the instability is triggered when a certain critical temperature rise of the neck above the ambient temperature is achieved.

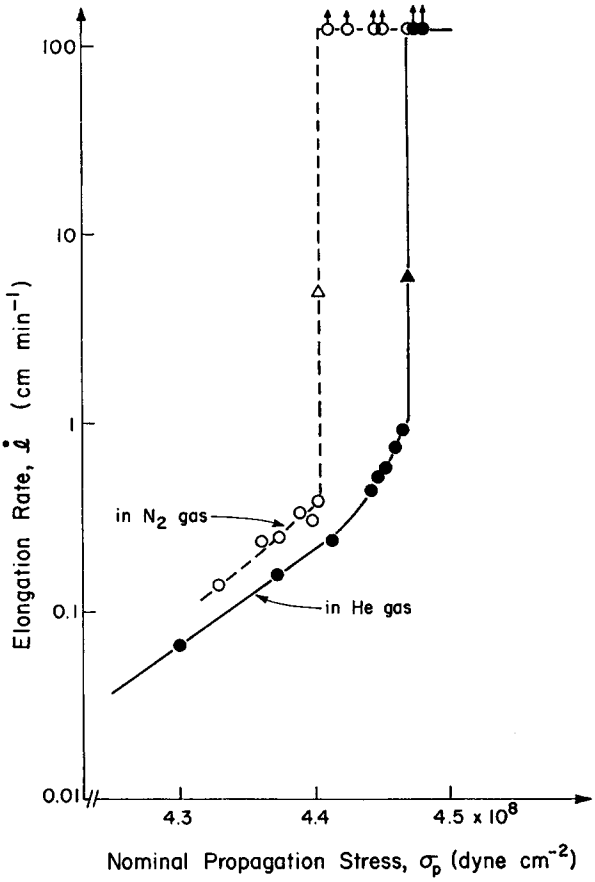
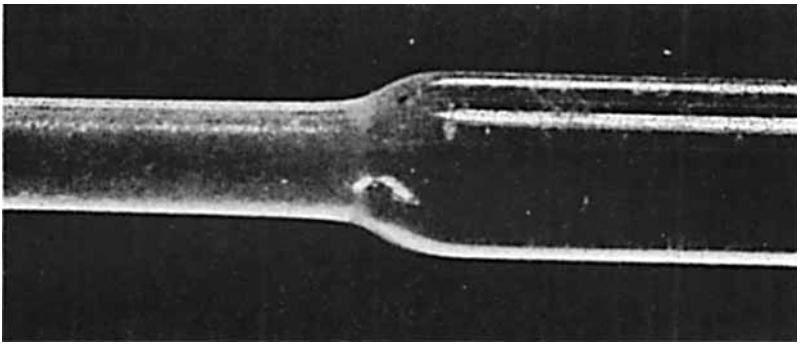
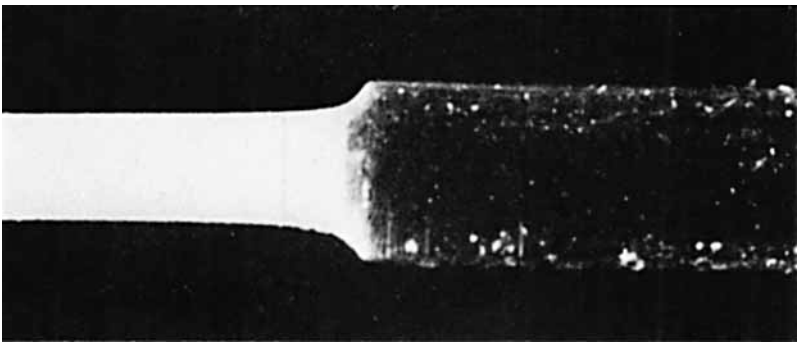


Fig. 1. Logarithm of elongation rate $\dot{l}$ versus stress σ_p in the unoriented filament. Gas temperature was 25.0°C; filled symbols represent drawing under He gas, open symbols, under N_2 gas. The elongation rate after runaway is difficult to measure precisely, so this condition is represented by a single $\dot{l}$. The actual $\dot{l}$ values are somewhat greater than 120 cm/min.

The structure of the drawn fiber produced by the runaway neck is completely different from that produced by stable neck propagation. Photographs of the shoulder region of a runaway neck and a stable neck are reproduced in Figure 2. The runaway neck is opaque, or "stress whitened," whereas the stable neck is transparent. It is likely that the opacity of the runaway neck is due to a microvoid structure, because its density is much less than even the density of completely amorphous nylon 6–10.[10]



(a)



(b)

Fig. 2. Photographs of drawn filament emerging from the shoulder (a) after stable neck propagation and (b) after thermal runaway.

Further evidence that this structure, and thus neck runaway, is due to heating at the shoulder is provided by an examination of how the opaque structure develops when the applied stress is raised from a stress that allows stable neck propagation to a stress which produces neck runaway. A photograph which shows the drawn fiber resulting from such a change in stress is displayed in Figure 3. It is apparent that the opaque structure originates in the center of the filament, the hottest portion, and spreads, as the neck motion and heating continues, to the outside. Note also that just before opaque structure nucleated, the draw ratio of the clear filament increased, decreasing the diameter of the drawn filament, which also indicates that the shoulder was heating. Step changes in stress below the critical neck velocity do not produce such large changes in draw ratio.

DISCUSSION

Any thermally activated process, such as conduction of a semiconductor junction or the motion of a neck during the cold drawing of nylon, which generates heat in proportion to its rate is subject to an instability called thermal runaway. Consider a neck which is subjected to a stress σ_p at ambient temperature T_p. The shoulder immediately begins to propagate

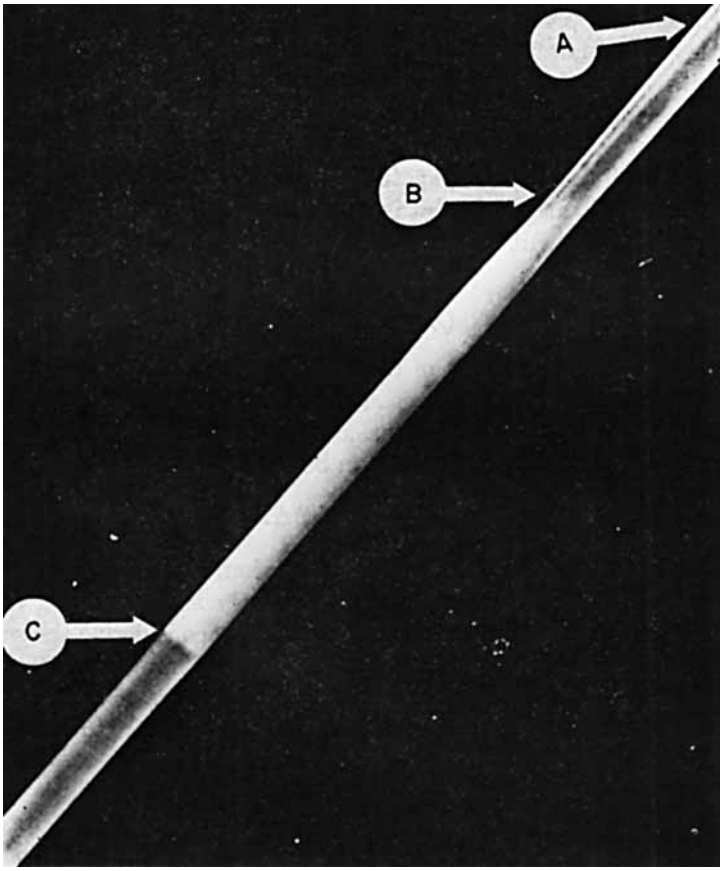


Fig. 3. Photograph of drawn filament after an increment of load that produces thermal runaway. Load was applied at A and was abruptly removed at C after thermal runaway had started at B. The direction of motion of the shoulder was from A to C.

(ignoring any complicating stress ageing effects[9]) at the v_n dictated by eq. (1) with $\sigma = \sigma_p$ and $T = T_p$. The plastic deformation, however, produces heat at a rate $\dot{Q}_{in} = \sigma_p A_u \dot{l}$ where A_u is the area of the unoriented fiber and $\dot{l} = (R - 1)v_n$. There will be a rise in temperature $\Delta T'$, the magnitude of which depends on the rate that heat is conducted away from the shoulder through the filament and the gas. This increase in T from T_p to $T_p + \Delta T'$ will produce, from eq. (1), an increase in the neck velocity $\Delta v_n'$, and this increase in neck velocity in turn will produce an additional increase in T, $\Delta T''$. If $\Delta T'' \ll \Delta T'$, the series solution for v_n converges, and stable neck propagation results. As $\Delta T''$ approaches $\Delta T'$, at some point the solution diverges, and stable neck propagation governed by eq. (1) is no longer possible under constant stress. Catastrophic heating and an abrupt change in the mode of deformation results. (Actually the heating is not as catastrophic as in the semiconductor case because the temperature rise is limited by the draw ratio of the drawn fiber formed during thermal runaway.)

It is possible to predict the critical neck velocity or elongation rate $\dot{l}_c$ at which thermal runaway occurs. In what follows, $\dot{l}_c$ is computed and compared with the $\dot{l}_c$ values measured experimentally. First, an expression for the temperature rise in the shoulder as a function of $\dot{l}$ is needed. This expression can be found by equating the power input $\dot{Q}_{in}$ to the rate of heat transfer through the solid $\dot{Q}_s$ plus the rate of heat transfer through the gas $\dot{Q}_g$ plus the rate $\dot{Q}_r$ at which heat is lost to the shoulder due to the motion of the heated drawn fiber from the shoulder. This last contribution is given by

$$\dot{Q}_r = A_u v_n C_p \Delta T \tag{3}$$

where C_p is the heat capacity of the nylon per unit volume and ΔT is the increase in the temperature of the shoulder above the ambient temperature. Following Vincent,[5] the heat transfer rate through the solid from the shoulder to the unoriented polymer can be estimated to be

$$\dot{Q}_s = (K_s A/w)\Delta T \tag{4}$$

where K_s is the thermal conductivity of nylon, A is the effective heat transfer area ($A < A_u$), and w is the width of the shoulder along the fiber axis. The heat transfer to the gas is estimated by considering the shoulder to be a sphere with a surface area equal to the approximate surface area of the shoulder, πwd, where d is the diameter of the undrawn filament. The steady-state heat transfer by conduction from such a sphere to a nonflowing gas is given by

$$\dot{Q}_g = 2\pi\sqrt{wd}K_g\Delta T \tag{5}$$

where K_g is the thermal conductivity of the gas. The numerical values of $\dot{Q}$ and the geometric and thermal constants that are necessary to compute them are given in Table I.

TABLE I
Heat Balance at the Shoulder of Drawing Neck and Values of Geometric and Thermal Parameters

Input	Through N_2 gas	Through He gas	Through nylon	Retained in drawn fiber	Units
$\dot{Q} = 55\dot{l}$	$1.25\Delta T$	$7.20\Delta T$	$7.3\Delta T$	$1.0\dot{l}\Delta T$	10^{-5} cal/sec
		(ΔT in °C, $\dot{l}$ in cm/min)			
$\sigma_p = 4.4 \times 10^8$ dyne/cm^2		K_s = 58×10^{-5} cal cm^{-1} sec^{-1} °C^{-1}			(ref. 11)
$A_u = 3.14 \times 10^{-3}$ cm^2		$K_g(N_2)$ = 6.2×10^{-5} cal cm^{-1} sec^{-1} °C^{-1}			(ref. 11)
$A = 2 \times 10^{-3}$ cm^2		K_g(He) = 36×10^{-5} cal cm^{-1} sec^{-1} °C^{-1}			(ref. 12)
$w = 1.6 \times 10^{-2}$ cm		C_p = 0.4 cal cm^{-3}			(ref. 11)
$R \simeq 3$					

The temperature rise ΔT is of the form

$$\Delta T = C_1 \dot{l}/(C_2 + \dot{l}) \tag{6}$$

where the $\dot{l}$ term in the denominator arises due to $\dot{Q}_r$ and limits the temperature rise at an infinite drawing rate to the rise that would result from adiabatic drawing, about 60°C. However, the measured $\dot{l}_c$ values are much less than the calculated C_2 values, so it will suffice for the purpose of this calculation of $\dot{l}_c$ to replace $\dot{l}$ in the denominator of eq. (6) by the measured value of $\dot{l}_c$. The temperature rise is then

$$\Delta T = C\dot{l} \tag{7}$$

where C is 6.2°C min/cm for nitrogen and 3.5°C min/cm for helium.

A convenient way to compute $\dot{l}_c$ is to consider a thought experiment where the stress σ is measured as a function of $\dot{l}$. (This is actually not a good experiment to measure $\dot{l}_c$ because the maximum is very broad and is easily masked by small variations in V^* and ΔH^* along the filament. Nevertheless maxima in σ from constant strain rate tests at approximately $\dot{l}_c$ have been observed for nylon 6–10.) There is a maximum in the stress at $\dot{l} = \dot{l}_c$ which corresponds to the $\dot{l}_c$ for thermal runaway in the constant stress experiment. By rearranging eq. (1), the stress σ is given by

$$\sigma = (4/V^*)\{\Delta H^* - k_B T \ln (\dot{l}_0/\dot{l})\} \tag{8}$$

since $v_n/v_0 = \dot{l}/\dot{l}_0$. The temperature T is given by

$$T = T_p + C\dot{l}. \tag{9}$$

If σ is maximized with respect to $\dot{l}$, $\dot{l}_c$ can be found to be

$$\dot{l}_c = T_p/C[\ln (\dot{l}_0/\dot{l}_c) - 1] \tag{10}$$

and since, from eq. (1), $\ln(\dot{l}_0/\dot{l}_c) = \Delta H^*_{\text{eff}}/k_B(T_p + \Delta T_c) \gg 1$ where ΔT_c is ΔT at $\dot{l}_c$, $\dot{l}_c$ can be written as

$$\dot{l}_c = k_B T_p(T_p + \Delta T_c)/C\Delta H^*_{\text{eff}}. \tag{11}$$

From the measured ΔH^*_{eff} and the calculated C values for N_2 and He, the critical elongation rates are found to be

$$\dot{l}_c = 0.34 \text{ cm/min} \qquad (N_2 \text{ gas})$$

and

$$\dot{l}_c = 0.60 \text{ cm/min} \qquad (\text{He gas}).$$

The critical temperature rise ΔT_c for thermal runaway is only 2.1°C.

These calculated values of $\dot{l}_c$ agree very well with the measured values, considering the crudity of the heat transfer model. The largest source of error is probably in the heat transfer rate to the gas, since it was assumed that the gas was static, whereas in this experiment it was actually flowing past the neck. In fact, if the gas heat transfer rates are both multiplied by a factor of 3, almost complete agreement of the calculated with the experimental values results.

The structure of the drawn fiber formed after thermal runaway also warrants some comment. It is well known that at high temperatures ($T \simeq 100°C$) the unoriented filament draws uniformly without neck formation. No opaque microvoid structure is formed under these conditions. On the other hand, during thermal runaway, only the local region of the shoulder is heated appreciably; it is plastically constrained by the cooler unoriented fiber. This plastic constraint results in a state of triaxial tension in the hot shoulder. Thus, two conditions, triaxial tension and a high local chain mobility (due to the high temperature of the shoulder), which might be expected to favor formation of a microvoid structure, are present. These are precisely the conditions that are thought to favor formation of the microvoid structure in the material in a craze.[13,14] It would be interesting to determine whether the microvoid structures formed under such different circumstances have similar properties and void distributions.

These observations are relevant to the interpretation of constant elongation rate test data. By using the analysis presented above, one can, from a measured value of the critical elongation rate for the onset of thermal runaway under constant load and a measured activation enthalpy for neck propagation, compute the effect of heating on the measured propagation stress, without making any assumptions about the geometry or rate of heat transfer. Also, because the plastic elongation rate can substantially exceed the elongation rate of the crosshead during a yield drop, drawn structures resulting from thermal runaway can form during a constant elongation rate test. Abrupt stress drops after the initial yield maximum (as an example, see ref. 7, Fig. 7) are indicative of thermal runaway. In nylon 6–10, thermal runaway followed by stress aging causes a curious "ringing"[15] of the stress after the yield point at high elongation rates.

The financial support of the Advanced Research Projects Agency through the Cornell Materials Science Center is gratefully acknowledged.

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Received August 3, 1970.