The Effect of Internal Temperature Rise on the Tensile Behavior of Polymeric Materials at Subambient Temperatures

J. SKELTON, W. D. FREESTON, JR., AND M. M. SCHOPPEE,

Fabric Research Laboratories, Inc., Dedham, Massachusetts 02026

Synopsis

The tensile properties of nylon, Dacron, and Nomex yarn are given at liquid helium temperatures, −450°F, and at two strain rates, 1.67 and 3000%/sec. The data are compared to similar results obtained at −320°, −109°, and 70°F. A theoretical analysis of the thermodynamics of straining under both isothermal and adiabatic conditions is presented, and theoretical maximum temperature rises occurring within both adiabatically and isothermally strained yarns are given for a range of subambient test temperatures. The initial modulus of the yarns increases, the tenacity increases, and the breaking elongation decreases with decreasing temperature at the lower rate of straining. However, at the higher rate of straining, although the initial modulus of the yarns at −450°F is considerably greater than the modulus at −320°F, the nylon yarn shows a lower breaking load and greater breaking elongation at −450°F than at −320°F. The Dacron follows the expected trend with the breaking load higher and the breaking elongation smaller at −450°F than at −320°F. The Nomex has a lower breaking load, but its breaking elongation is also lower at −450°F than at −320°F. The calculated yarn internal temperature rises are sufficient to explain these differences in the stress–strain behavior of the yarns.

INTRODUCTION

Previous measurements of the tensile behavior of polymeric yarns at high rates of strain and subambient temperatures[1] suggested that at sufficiently low ambient temperatures the adiabatic extension of these materials might bring about large temperature rises within the polymer, with a consequent effect on the load–elongation response. In an effort to verify this point, the thermodynamics of straining were analyzed theoretically in order to predict the magnitude of possible temperature rises within the polymer which might occur as the result of adiabatic straining. The analysis takes into account changes in the specific heat and modulus of the material with temperature.

A series of tensile tests was also carried out on polymeric materials under both isothermal and adiabatic conditions at liquid helium temperatures (−454°F). The investigation was confined to three materials, nylon, Dacron, and Nomex yarns, and to two strain rates, 1.67%/sec and 3000%/

sec. These strain rates were chosen in the hope that they would adequately represent isothermal and adiabatic straining, respectively. Theoretical calculations indicate that the high strain rate tests are indeed almost completely adiabatic. Some temperature rise occurs at the lower strain rate, but it is sufficiently small that these tests can be considered approximately isothermal.

Both the theoretical analysis and the experimental results indicate that for some materials the temperature rise has a significant effect on their tensile behavior.

EXPERIMENTAL

The tensile tests at 1.67%/sec and 3000%/sec involved the use of the Instron tensile tester and the FRL small piston tester[1] respectively.
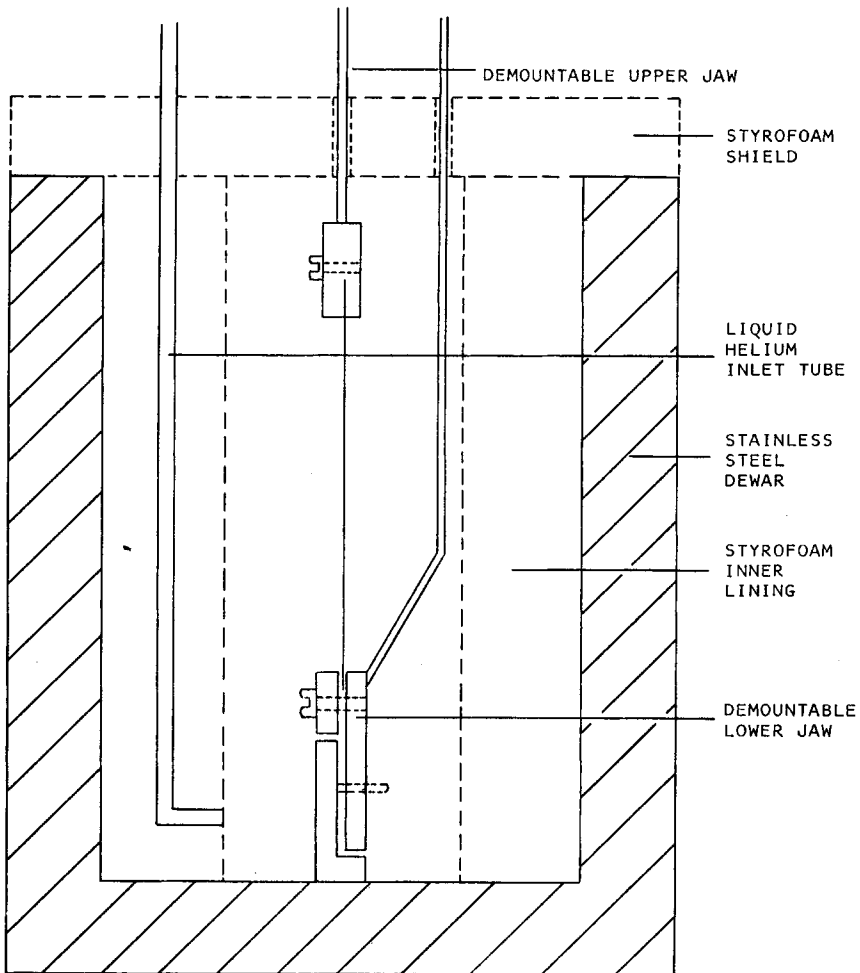

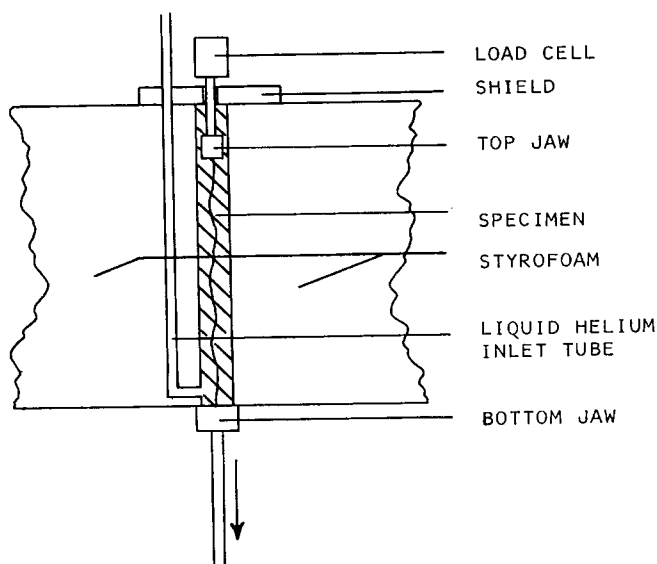Fig. 1. Low-temperature environmental chamber for use with Instron.

Fig. 2. Low-temperature environmental chamber for use with high-speed piston tester.

Environmental chambers for these testers suitable for use with liquid nitrogen and a solid–gaseous mixture of CO_2 as refrigerants were fully described by Skelton and co-workers[1]; attempts to maintain a level of liquid helium, obtained from a helium Dewar equipped for liquid phase withdrawal, within these chambers was not successful. However, temperature measurements within the chambers made with a copper–Constantan thermocouple calibrated in liquid helium showed that the stream of cold gas and liquid droplets emerging from the transfer tube could quickly produce and maintain a temperature of less than $-448°F$ within the test chamber. Brief descriptions of the chambers are given below.

The experimental arrangement used with the Instron tester is shown diagrammatically in Figure 1. The chamber is a stainless steel Dewar which is attached to the crosshead of the Instron. A Styrofoam inner lining reduces the volume to be cooled. The chamber is equipped with a special jaw system. A post with a peg upon which the demountable lower jaw assembly locates is attached to the bottom of the vessel. The lower jaw assembly is provided with an insulated handle so that it can be mounted and demounted in the presence of refrigerant. A detachable upper jaw assembly is suspended from the load cell. The appropriate length of material under test is mounted between the detached upper and lower jaw assemblies; the bottom jaw is located on the fixed peg; and the upper jaw is connected to the Instron load cell. The cold helium gas is then passed through an entry port at the bottom of the chamber, and the temperature within the chamber is measured with a copper-Constantan thermocouple. The load cell is protected from the cold exhaust gas stream by a Styrofoam shield.

The experimental arrangement used with the FRL piston tester is shown diagrammatically in Figure 2. The chamber consists of a block of Styrofoam which is located between the top and bottom jaws of the tester and through which a $1/2$-in.-diameter hole has been bored. The specimen under test is mounted in the jaws, then the bottom jaw is moved up to press tightly against the bottom of the Styrofoam to seal the chamber. As with the Instron chamber, the cold helium gas is passed through an entry port at the base of the chamber and the load cell is protected by a Styrofoam shield.

The test procedure was essentially the same for both experimental arrangements. Following mounting of the specimen at room temperature, the mixture of liquid and gaseous helium was passed into the chamber and the temperature was continuously monitored. Equilibrium conditions were generally reached within the temperature range of $-447°F$ to $-452°F$, and the tensile tests were carried out under these conditions. Table I gives details of the yarns tested and the test conditions. For both series of tests the specimens were mounted in flat, tape-lined jaws. For the Instron tests a 5-in. gauge length and a jaw speed of 5 in./min. were used, giving a strain rate of 1.67%/sec; for the piston tester a gauge length of 22 in. and a jaw speed of approximately 60 ft/sec were used, giving a strain rate of approximately 3000%/sec.

TABLE I
Details of Yarns Tested and Test Conditions

Mate- rial	Yarn	Mea- sured denier	Strain rate, %/sec	Temp. range, °F
Nylon	1050–175–1/2Z, Type 702[a]	1040	1.67; 3,000	−447 to −452
Dacron	1100–250–0, Type 52[a]	1060	1.67; 3,000	average for all
Nomex	1200–600–0, Type E-1[a]	1280	1.67; 3,000	tests −450

[a] E. I. du Pont de Nemours and Co.

RESULTS

Test results obtained at the liquid helium temperatures are given in Tables II, III, and IV. These tables also include results from the previous investigation for the properties of these materials at other temperatures.

Typical stress–elongation diagrams for the three materials tested at $-450°F$ are shown in Figures 3, 4, and 5, which also include for comparison the tensile behavior at $-320°F$. For all materials at both high and low strain rates, the initial modulus at $-450°F$ is considerably greater than the modulus at $-320°F$ and is in excellent agreement with the modulus-temperature variation previously found (see Fig. 6). This is in accord with theoretical expectations, since no internal temperature rise is expected for the low values of strain at which the initial modulus is measured. However, as the amount of energy supplied to the specimen increases, the

TABLE II
Tensile Properties of Nylon Yarn at
Various Strain Rates and Temperatures

Temp., °F	Tenacity, g/den		Rupture elongation, %		Initial modulus, g/den	
	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec
−450	13.2	10.3	8.9	7.9	278	319
−320	12.9	10.9	10.8	7.3	211	234
−109	11.1	8.7	12.7	8.4	98	86
+70	7.61	8.80	19.8	13.9	39.6	48

TABLE III
Tensile Properties of Dacron Yarn at
Various Strain Rates and Temperatures

Temp., °F	Tenacity, g/den		Rupture elongation, %		Initial modulus, g/den	
	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec
−450	11.1	10.7	8.8	7.3	255	410
−320	11.6	10.5	10.1	8.0	231	238
−109	10.1	8.7	11.2	10.4	166	130
+70	7.45	8.80	15.6	12.7	93.5	148

TABLE IV
Tensile Properties of Nomex Yarn at
Various Strain Rates and Temperatures

Temp., °F	Tenacity, g/den		Rupture elongation, %		Initial modulus, g/den	
	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec	1.67%/ sec	3000%/ sec
−450	6.6	5.4	4.1	3.1	189	263
−320	7.52	6.92	7.1	4.4	178	184
−109	6.73	5.77	18.5	6.8	131	142
+70	4.81	5.20	27.8	23.2	114	150

stress–elongation diagram for the high strain rate curves change in character, and the materials behave as if they were at a much higher temperature. In particular, the nylon and Dacron yarns, which have a work-to-rupture parameter greater than that of the Nomex yarn, show marked evidence of a yield at high rates of strain (see curve 4 in Figs. 3 and 4). As a consequence, the nylon yarns show a lower breaking load and greater breaking elongation at −450°F than at −320°F. The Dacron has a very high initial modulus at −450°F, and in spite of the pronounced yield has a higher breaking load and smaller breaking elongation at −450°F than at −320°F. The Nomex has a lower breaking load, but its breaking elongation is also lower at −450°F than at −320°F. The detailed high strain

rate response of a particular material at very low temperatures is evidently
dependent on the shape of its load–elongation diagram: the greater the
work to rupture, the more the material will be affected by the decrease
in its specific heat at low ambient temperatures and the greater will be the
effect on its tensile response.

The values of initial modulus, tenacity, and breaking elongation at low
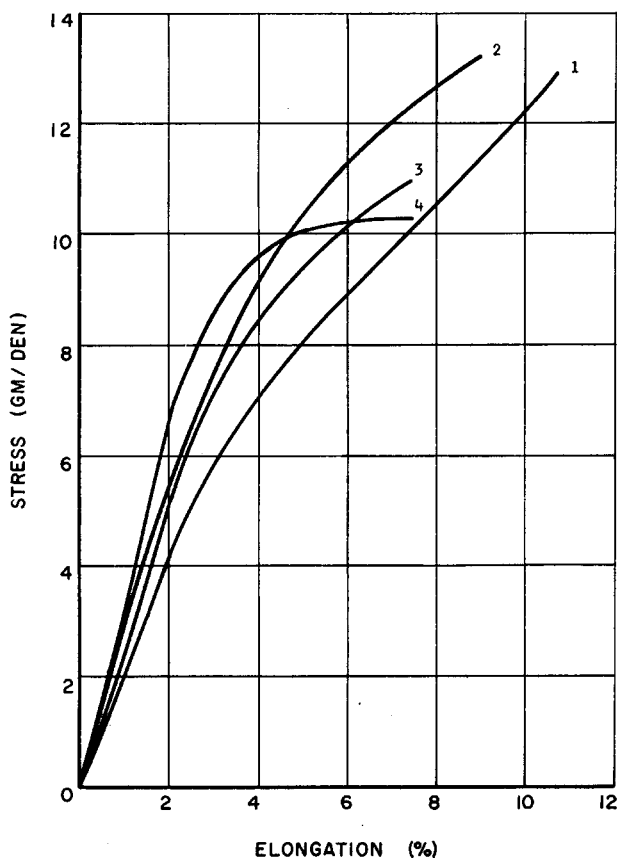strain rates follow expected trends (see Figs. 6, 7, and 8); the modulus

Fig. 3. Stress–elongation diagrams for nylon yarn at various strain rates and tempera-
tures.   (1) 1.67 %/sec, −320°F; (2) 1.67 %/sec, −450°F; (3) 3000 %/sec, −320°F;
(4) 3000 %/sec, −450°F.

increases, the tenacity increases, and the breaking elongation decreases
with decreasing temperature.   There is no evidence of yielding in the
response of the nylon and Dacron.   This emphasizes the fact that yielding
for these materials at high strain rates at −450°F is a phenomenon asso-
ciated solely with the adiabatic strain conditions and does not reflect
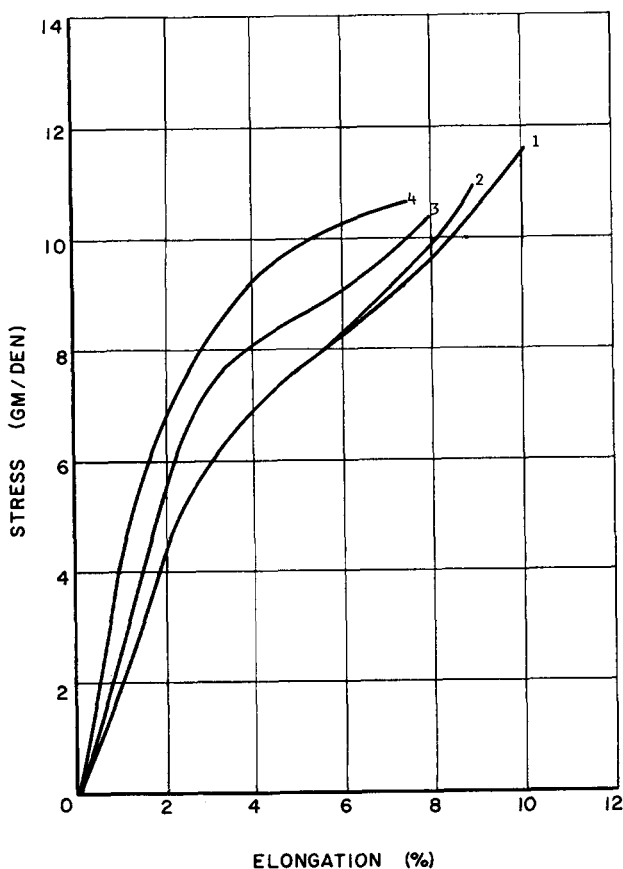structural changes at the molecular level.

Fig. 4. Stress–elongation diagrams for Dacron yarn at various strain rates and temperatures. (1) 1.67 %/sec, −320°F; (2) 1.67 %/sec, −450°F; (3) 3000 %/sec, −320°F; (4) 3000 %/sec, −450°F.

Theoretical Discussion

Theoretical analyses of the thermodynamics of strained yarns have been made by Hall[2] and by Meredith;[3] these have been concerned with the temperature rise above an ambient temperature of 70°F. The analysis herein follows that of Hall, though several modifications have been made to take into account the variations of specific heat and modulus with temperature.

Consider a homogeneous cylindrical filament of length L cm. Let the filament be extended dL cm in a time interval dt sec by a force F dynes. Let the filament be at a uniform temperature $T°K$; as a result of the work done in extending the filament, this temperature is higher than that of the surroundings $T_0°K$.

Arthur and Jones[4] have shown that the temperature gradient within a typical textile yarn is negligible for a temperature differential across the
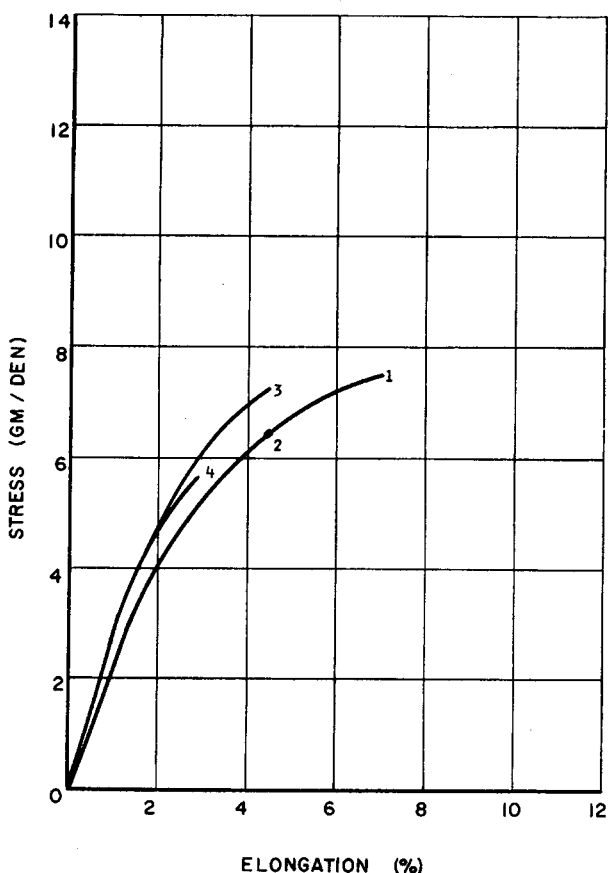
Fig. 5. Stress–elongation diagrams for Nomex yarn at various strain rates and tempera-
tures.   (1) 1.67 %/sec, −320°F; (2) 1.67 %/sec, −450°F; (3) 3000 %/sec, −320°F;
(4) 3000 %/sec, −450°F.

boundary of the yarn of up to 500°C (∼900°F) due to the large surface-
to-volume ratio characteristic of a bundle of small-diameter fibers.   Thus,
the assumption of uniformity of temperature in the present analysis
is reasonably justified so long as the thermal conductivity of the polymeric
material does not become vanishingly small at very low temperatures.

Eiermann and Mellwege[5] have shown that the thermal conductivity
of polymers is almost independent of temperature over the range −320°F
to +70°F.   At lower temperatures, the thermal conductivity of polymers
decreases with decreasing temperature,[6] and at −450°F its value is approxi-
mately one tenth that at higher temperatures.   This reduction is signif-
icant but is not sufficient to invalidate the assumption of temperature
uniformity within the filament.

Let the filament lose a quantity of heat dQ calories to the surroundings
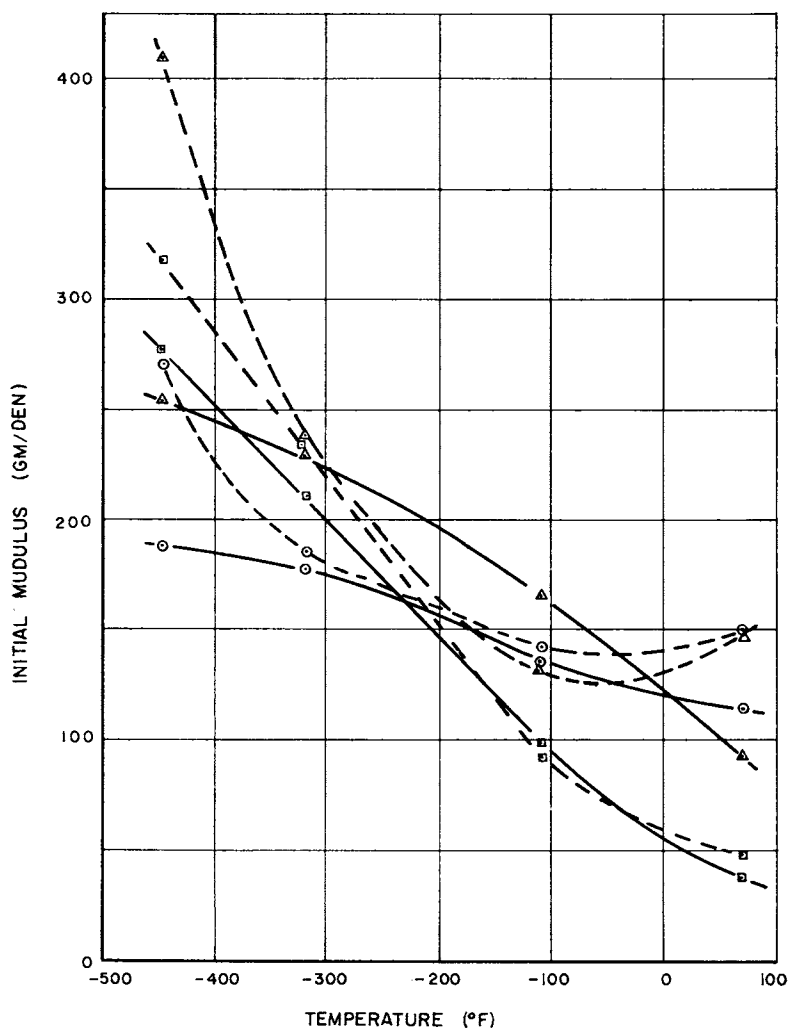during the interval dt.   If the deformation takes place at constant volume,

Fig. 6. Variation of yarn initial modulus with temperature for two strain rates. (□) nylon; (△) Dacron; (⊙) Nomex; (—) 1.67 %/sec; (---) 3000 %/sec.

then the change in internal energy dU calories of the filament may be written

$$dU = (0.24 \times 10^{-7})F dL - dQ. \tag{1}$$

If changes in filament radius are neglected and the internal energy U is considered to be a function only of L and T, then

$$dU = (\partial U/\partial L)_T dL + (\partial U/dT)_V dT = (\partial U/\partial L)_T dL + C_V dT \tag{2}$$

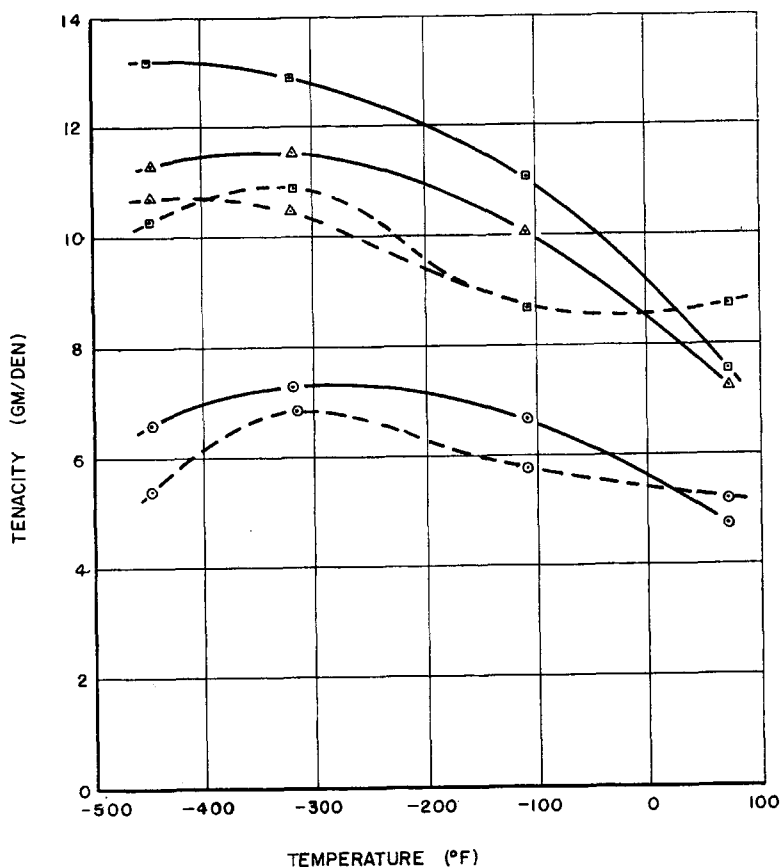where C_V is the heat capacity, in cal/°K, of the filament at constant volume.

Fig. 7. Variation of yarn tenacity with temperature for two strain rates. (□) nylon; (△) Dacron; (⊙) Nomex; (—) 1.67 %/sec; (---) 3000 %/sec.

Thus,

$$[0.24 \times 10^{-7}F - (\partial U/\partial L)_T]dL = C_V dT + dQ. \tag{3}$$

The term $(\partial U/\partial L)_T$ in eq. (3) represents the rate of change of internal energy at constant temperature with respect to extension. It varies in magnitude, in the appropriate units, from zero for ideal rubber-like material (in which the extension brings about changes only in entropy) to $0.24 \times 10^{-7}F$ for highly crystalline materials (which have only a small change in entropy with extension). It also varies with temperature, strain, and strain rate. As a simplification, the first term in eq. (3) may be written

$$[0.24 \times 10^{-7}F - (\partial U/\partial L)_T]dL = 0.24 \times 10^{-7}kFdL \tag{4}$$

in which the constant k may be chosen to suit the conditions of a particular test. Thus, a value of $k = 1$ implies that all the work done in extending the yarn appears as heat, while a value of $k = 0$ implies that no work appears as heat.
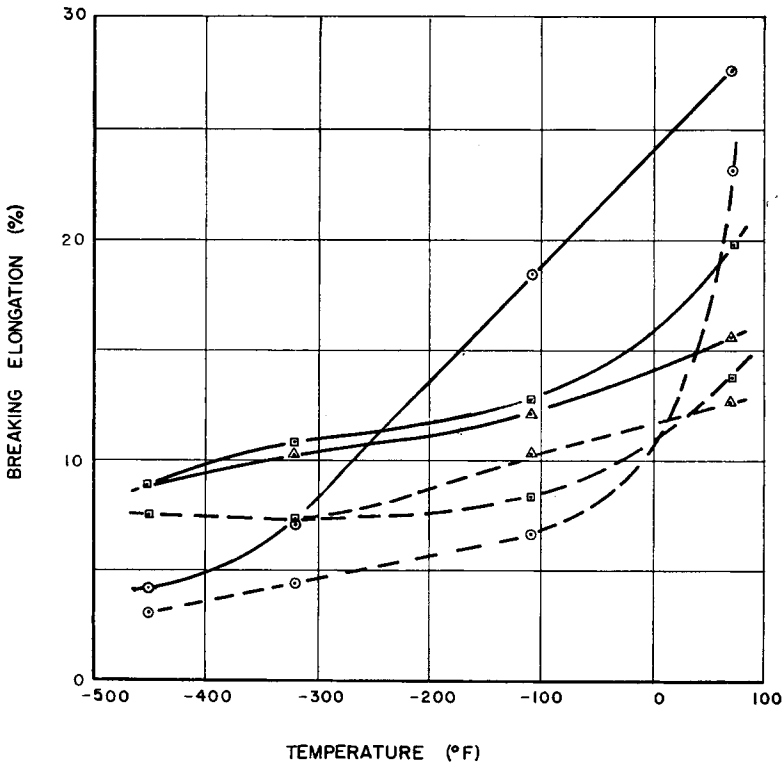
Fig. 8. Variation of yarn rupture elongation with temperature for two strain rates. (□) nylon; (△) Dacron; (⊙) Nomex; (−) 1.67 %/sec; (---) 3000 %/sec.

Thus, eq. (3) may be written as follows:

$$0.24 \times 10^{-7} kFdL = C_V dT + dQ. \tag{5}$$

The amount of heat dQ lost to the surroundings in the time interval dt is given by Newton's law of cooling:

$$dQ = 2\pi r L H (T - T_0) dt \tag{6}$$

where r is the radius of the filament in centimeters and h is the heat transfer coefficient in cal/cm² °C sec.

Writing the force F dynes in terms of textile units gives

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

where f is the specific stress in g/denier and ρ_L is the linear density of the filament in denier. Since the denier is the weight of 9000 meters of filament,

$$\rho_L = 9 \times 10^5 \rho \pi r^2 \tag{8}$$

where ρ is the density of the material in g/cm³.

Changes in length, dL, are usually expressed as changes in percentage strain, $d\epsilon$:

$$dL = Ld\epsilon/100. \tag{9}$$

Substituting eqs. (6), (7), (8), and (9) into eq. (5) and writing C_V in terms of c_V, the specific heat per unit weight of material, gives the following:

$$0.24\times10^{-7}k\ 981f\rho_L\frac{Ld\epsilon}{100} = c_V\frac{L\rho_L dT}{(9\times10^5)} +2\rho_L h$$
$$\times\left[\frac{\pi}{(9\times10^5\rho\rho_L)}\right]^{1/2}(T-T_0)Ldt. \tag{10}$$

Writing $d\epsilon/dt = \dot\epsilon$, the strain rate in %/sec, taking $\rho = 1$ as a reasonable value for textile yarns,[4] evaluating the numerical constants, and rearranging terms gives the following:

$$c_V(dT/d\epsilon) + 3.4\times10^3\frac{h(T-T_0)}{\rho_L^{1/2}}\dot\epsilon = 0.21kf. \tag{11}$$

This corresponds to Hall's eq. (12).

At low temperatures, the specific heat of polymeric materials is principally a function of the temperature. The specific heat at constant volume c_V and the measured specific heat at constant pressure c_P are related by the equation

$$c_P - c_V = VT\alpha^2/\beta \tag{12}$$

where V is the volume of 1 g of material, α is the volume coefficient of thermal expansion, and β is the compressibility at pressure P. It is usually assumed that $c_P - c_V$ is negligibly small and that c_P may be used interchangeably with c_V.

Melia[7] in a review article discusses the temperature variation of the specific heats of polymeric material. For most polymeric materials, the specific heat is approximately proportional to the absolute temperature over a wide range of temperature; moreover, the constant of proportionality is approximately the same for all polymeric materials. This relationships may be written as follows:

$$c_V = c_P = T/600. \tag{13}$$

In order to use eq. (11) for numerical estimates, a value must be found for the heat transfer coefficient h. Hall uses a value of 3.2×10^{-3} cal/cm^2 °C sec, taken from the work of Arthur and Jones[4]; this work also shows that the heat transfer coefficient to air is independent of temperature over the range 20°–500°C (70°–~900°F). Seader and co-workers[8] carried out an extensive survey of heat transfer to boiling cryogenic liquids. They found that the heat transfer coefficient varies with the nature of the boiling process, which in turn depends on the temperature difference between the

heated element and the body of the liquid. A reasonable value of h for heat transfer from metal surfaces to liquid nitrogen for the range of temperature difference appropriate to the present application is 13.6×10^{-3} cal/cm^2 °C sec. The heat transfer to helium gas and to a solid/gaseous mixture of CO_2 is likely to be somewhat less and is probably reasonably close to the Arthur and Jones value. Accordingly, the value of 3.2×10^{-3} cal/cm^2 °C sec has been chosen for the calculations outlined below, with the reservation that it might be too small by a factor of 4 for the liquid-nitrogen-cooled material.

The specific stress at any strain ϵ is given by

$$f = \int_0^\epsilon E_T d\epsilon / 100 \tag{14}$$

where E_T is the tensile modulus of the material in g/denier at the appropriate temperature T. It is assumed that the stress–strain curve of the material is linear in the absence of temperature rise; this is a reasonable assumption for most polymeric materials at low temperatures, particularly at high strain rates. The initial modulus of the polymeric materials studied is strongly dependent on the temperature T. Experimental results are given in Figure 6. The variation of modulus with temperature for any of the materials can be reasonably approximated by a linear function of the type

$$E_T = E_0[1 - (T/T_V)] \tag{15}$$

where E_0 is the value of initial modulus at 0°K and T_V is the temperature at which the line representing the modulus variation intercepts the temperature axis.

Substituting eqs. (13), (14) and (15) into eq. (11) and using the appropriate value for h gives

$$T(dT/d\epsilon) + [6.5 \times 10^3(T - T_0)/(\rho_L^{1/2}\dot{\epsilon})] = 1.2kE_0 \int_0^\epsilon [1 - (T/T_V)]d\epsilon. \tag{16}$$

TABLE V
Values of Numerical Parameters for Various Test Conditions

	Nylon	Dacron	Nomex
ρ_L, den	1040	1080	1280
E_0, g/den	297	277	212
T_V, °F	160	361	583
T_V, °K	344	456	579
T_0, °F		$-450; -320; -109; 70$	
T_0, °K		$5; 78; 195; 294$	
$\dot{\epsilon}$, %/sec		$1.67; 3,000$	
k (dimensionless)		1	

Differentiating with respect to ϵ, rearranging, and dividing through by T gives finally

$$d^2T/d\epsilon^2 = 1.2kE_0[(1/T) - (1/T_V)] - [(6.5\times10^3)/(\rho_L^{1/2}\dot{\epsilon})](1/T)(dT/d\epsilon)$$
$$- (1/T)(dT/d\epsilon)^2 \quad (17)$$

where $T = T_0$ at $\epsilon = 0$. This equation defines the relationship between the temperature (°K) in the stressed yarn and the strain (%) at any instant. It cannot be solved analytically in closed form, but has been
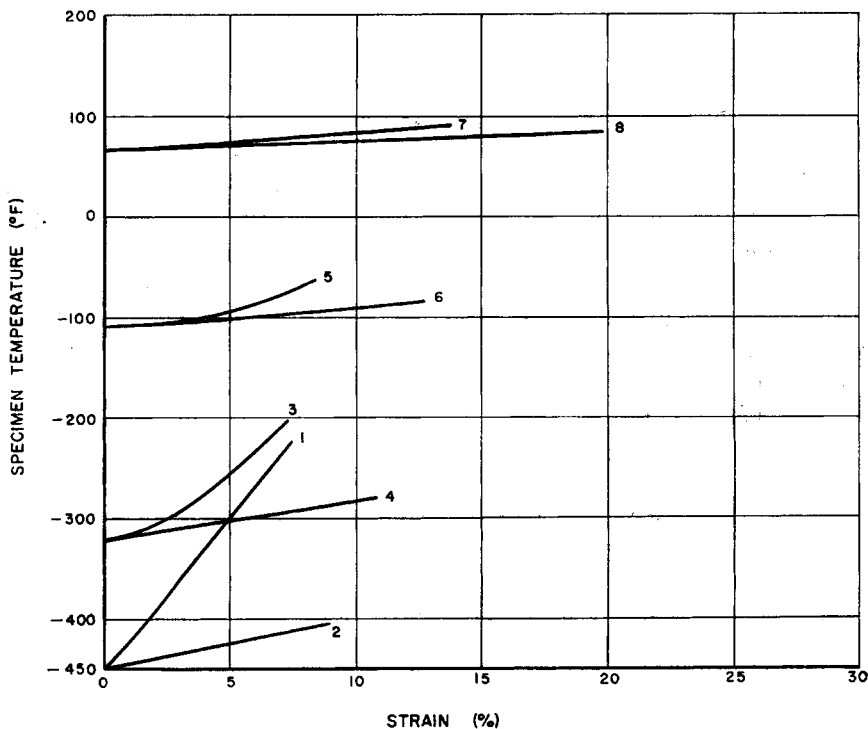

Fig. 9. Variation of yarn temperature with strain, strain rate, and test temperatures for nylon yarns. (1) −450°F, 3000 %/sec; (2) −450°F, 1.67 %/sec; (3) −320°F, 3000 %/sec; (4) −320°F, 1.67 %/sec; (5) −109°F, 3000 %/sec; (6) −109°F, 1.6%/(7) 70°F, 3000 %/sec; (8) 70°F. 1.67 %/sec.

solved numerically for the three materials tested for various initial temperatures and strain rates. The constants appropriate to the various materials are given in Table V.

Figures 9, 10, and 11 show the variation of temperature rise with strain for the three materials at various ambient temperatures and two rates of straining. The curves have been carried to strain levels equal to the measured breaking elongations. The maximum temperature rise within the specimens for tests carried out at 70°F is approximately 20°F for the nylon and 50°F for the Dacron yarns, values that are in good agreement
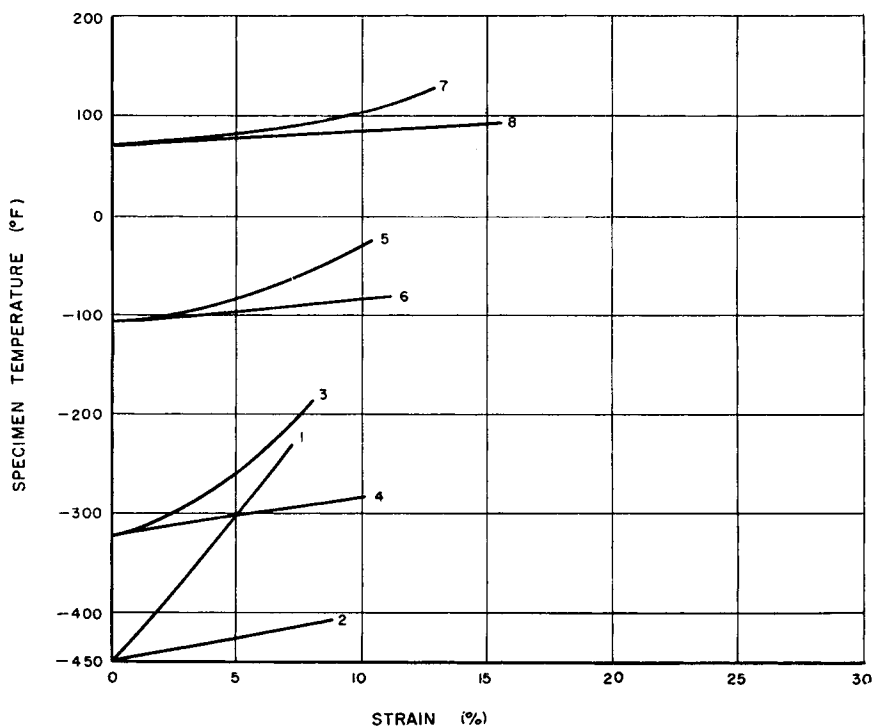
Fig. 10. Variation of yarn temperature with strain, strain rate, and test temperatures for Dacron yarns. (1) −450°F, 3000 %/sec; (2) −450°F, 1.67 %/sec; (3) −320°F, 3000 %/sec; (4) −320°F, 1.67 %/sec; (5) −109°F, 3000 %/sec; (6) −109°F, 1.67 %/sec; (7) 70°F, 3000 %/sec; (8) 70°F, 1.67 %/sec.

with Hall's calculations. For Nomex yarn, which even at high strain rates has a large breaking elongation, the temperature rise is 160°F.

The rate of internal temperature increase with strain increases for all the materials as the ambient temperature decreases, but the Nomex suffers a considerable reduction in breaking elongation with decreasing test temperature; consequently, the absolute magnitude of the maximum temperature rise within the yarn is quite small even at ambient temperature of −450°F. The nylon and Dacron, in contrast, have high breaking elongations even at very low temperatures, and the maximum temperature rise in these materials is approximately 220°F at ambient temperatures of −450°F. Indeed, as the theoretical curves demonstrate, the difference between the final temperature for tests carried out at −320°F and −450°F is only 20°F for nylon and 40°F for Dacron. This explains the marked differences observed experimentally between the form of the tensile stress–elongation curves for these two materials and the close similarity in the endpoints of the curves at the two temperatures.

A value of $k = 1$ was used for the calculations described above. This implies that all the work done in extending the specimens appears as heat,
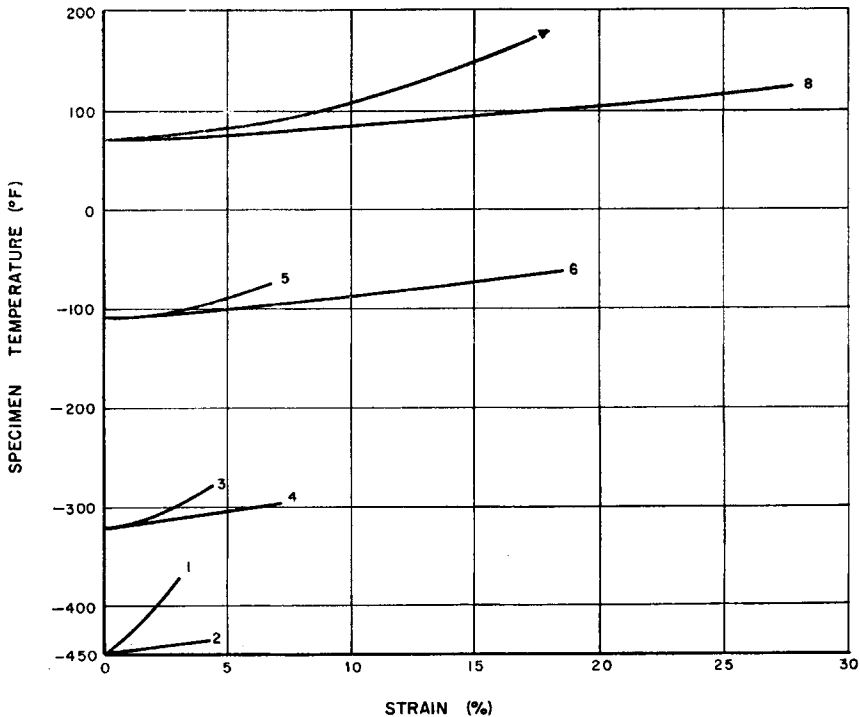
Fig. 11. Variation of yarn temperature with strain, strain rate, and test temperatures for Nomex yarns. (1) $-450°F$, 3000 %/sec; (2) $-450°F$, 1.67 %/sec; (3) $-320°F$, 3000 %/sec; (4) $-320°F$, 1.67 %/sec; (5) $-109°F$, 3000 %/sec; (6) $-109°F$, 1.67 %/sec; (7) 70°F, 3000 %/sec; (8) 70°F, 1.67 %/sec.

and accordingly the calculated values of temperature rise are theoretical maximum values. In practice, the value of k is not constant during the course of a test but probably approaches unity from an initial low value as the temperature and strain levels increase and the fraction of recoverable work decreases. In order to check the sensitivity of the temperature rise to this parameter, the calculation was carried out for nylon yarn at 3000%/sec and $-450°F$ with values of k of 0.2, 0.4, 0.6, 0.8, and 1.0. The results for strains up to 8% are plotted in Figure 12, from which it may be seen that the temperature rise is relatively insensitive to changes in k, particularly for high values of k, since the fivefold change in k produces only a twofold change in temperature rise. Thus, the previously calculated values of temperature rise, though possibly high, are probably quite close to the actual values within the strained yarns.

The other parameter whose value is not precisely known in the theoretical analysis is the heat transfer coefficient h. A value of 3.2×10^{-3} cal/cm² °C sec was used for all materials and experimental conditions. The temperature rise calculation was carried out for nylon yarn at 3000%/sec and $-450°F$ with values of the heat transfer coefficient of 32×10^{-3}
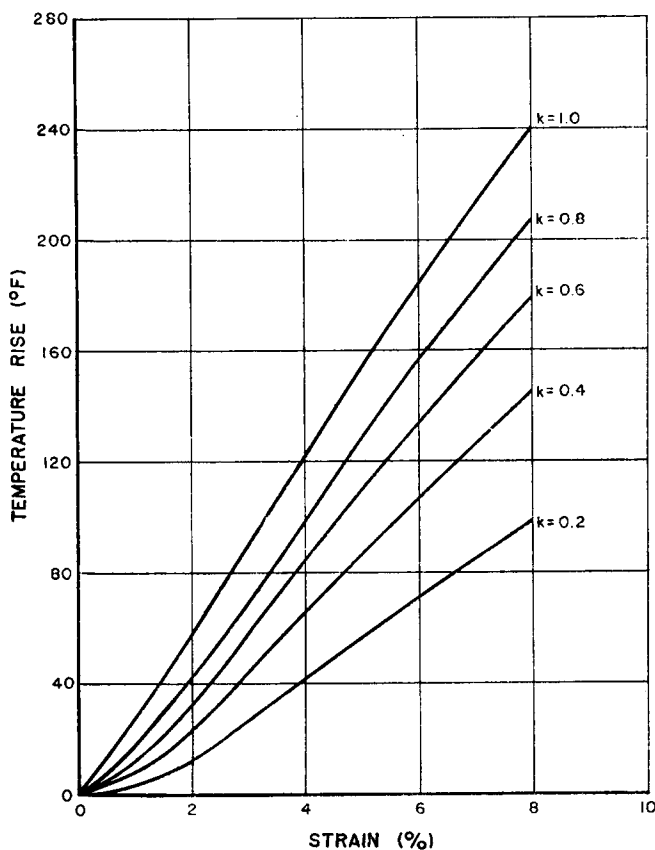
Fig. 12. Variation of temperature rise with strain for a range of values of k for nylon yarn at $-450°F$ and $3000\%/sec.$

and 0.32×10^{-3} cal/cm² °C sec. Changes of this magnitude had no detectable effect on the calculated values of temperature rise, demonstrating the complete insensitivity of the system to this parameter at high strain rates.

Conclusions

It has been shown that decreasing the ambient temperature from $-320°F$ to $-450°F$ has a large effect on the initial modulus of polymeric materials, particularly at high strain rates. Theoretical calculations indicate that very large temperature rises can occur within polymeric materials strained at high strain rates at very low ambient temperatures. The temperature rise minimizes the effect of ambient temperature on the endpoints of the load–elongation curve, though the shape of the load–elongation curve is profoundly modified at very low ambient temperatures. This finding is of considerable practical importance, since it ensures that the dynamic energy

absorbing capacity of a polymeric material is maintained even at very low ambient temperatures.

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