

Kinetics for the Tensile Strength Degradation of Nylon and Kevlar Yarns*

I. AUERBACH, *Aerodynamics Department, Sandia National Laboratories, Albuquerque, New Mexico 87185*

Synopsis

The tensile strength degradation of nylon 66 and Kevlar 29 yarns was studied at elevated temperatures and over a broad range of relative humidities. The degradation rates for nylon are initially slow but increase rapidly, suggesting the depletion of an inhibitor. Kevlar showed no evidence for similar inhibitor action. The effect of relative humidity on degradation can be very large, especially at values in the 90–100% range and at elevated temperatures. Degradation is governed by thermal-oxidative and moisture-induced mechanisms. At the very high humidities and elevated temperatures, the moisture-induced degradation predominates. Rate relationships were developed in which contributions from each mechanism were considered. Calculated degradation from these relationships agrees well with observed degradation over a broad range of temperatures and humidities.

INTRODUCTION

A need existed for estimating the safe and useful lifetime of devices such as parachutes that are fabricated from nylon and Kevlar yarns. A literature survey on parachute aging, however, did not provide definitive information that could be used for predicting aging. Consequently, a study was initiated to determine tensile strength degradation under accelerated aging conditions.

The objective of this study was to obtain estimates of the tensile strength degradation for nylon 66 and Kevlar 29 yarns used in parachute fabrication after exposure for extended time periods at ambient temperatures and variable humidity in the absence of light. To obtain these estimates, experimental degradation data were modeled with rate expressions that included concentrations terms for the presence of humidity and inhibitors. Rate constants were computed from these expressions and kinetic parameters calculated that permitted extrapolation of the degradation rate to ambient conditions.

A more detailed description of the experimental procedures given below as well as results on the effects of smog and ozone are given in a report by Mead et al.¹ The experimental data used in this report were obtained from that reference.

EXPERIMENTAL

Materials

The study was performed with yarn samples of 210 denier nylon 66 and 1500 denier Kevlar 29. These were machine-twisted two turns per inch, and

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TABLE I
Test Matrix for Relative Humidity Experiments

Material	Atmosphere on initial loading	Storage time (months)			Storage time (months)			Storage time (months)				
		2	4	6	2	4	6	2	3	4	6	
		110°C			130°C			150°C				
Nylon 66	0% RH air								X			
	10% RH air	X	X	X	X	X	X	X		X	X	
	50% RH air	X	X	X	X	X	X	X		X	X	
	90% RH air								X			
		130°C			150°C			170°C				
Kevlar 29	0% RH air								X			
	10% RH air	X	X	X	X	X	X	X		X	X	
	50% RH air	X	X	X	X	X	X	X		X	X	
	90% RH air								X			

represented typical yarns used in weaving narrow fabrics for ribbon parachute fabrication. Both yarns were obtained from DuPont and were treated with standard weaving finishes. Enough yarn (approximately 30 yards) for 10 unknotted and 10 knotted yarn test samples was wound on glass spools designed to fit into canisters for aging. The knotted samples were used to simulate tightly folded fabrics in a parachute pack.

Environmental Chambers

Sample containers for the elevated temperature-humidity experiments were fabricated from stainless steel tubing closed at one end and welded at the other end to a Conflat Type vacuum flange. A steel bellows valve for gas sampling was attached to a second flange.

Test Matrix

Samples were tested at five relative humidities (RH). One set of four samples was equilibrated in canisters at 0, 10, 50, and 90% relative humidities measured at 25°C. These values correspond to moisture concentrations of 0, 0.231, 1.153 and 2.075×10^{-5} g/cm³, respectively. The canisters were sealed

TABLE II
Samples Exposed at 100% RH for 2 Weeks

Test temp. (°C)	Material	Atmosphere
90	Nylon	Helium
	Kevlar	Helium
110	Nylon	Air
	Nylon	Helium
	Kevlar	Air
	Kevlar	Helium

before being subjected to elevated temperatures. Thus, for a given sample set, the amount of water in each canister was constant. The test matrix for this part of the study is shown in Table I.

A second set of samples was sealed in canisters with test tubes containing enough water to guarantee 100% relative humidity at aging temperature. One set was filled with air, the other with an inert gas. Using an inert gas for part of the experiments allowed comparisons of the degradation due to moisture alone with the combined degradation due to moisture and oxygen. The conditions are given in Table II.

RESULTS AND DISCUSSIONS

Degradation Kinetics

An initial analysis of high temperature tensile strength degradation data was made using Kevlar 29 data from the DuPont Product literature.² It covered the temperature range of 160–250°C and indicated that the degradation could be modeled with the following empirical second-order rate relationship and its integrated form:

$$-\frac{d\sigma}{dt} = k_a \sigma^2$$
$$k_a t = \frac{1}{\sigma} - \frac{1}{\sigma_0} \quad (1)$$

where σ = tensile strength at time t , σ_0 = initial tensile strength, and k_a = rate constant. In the latter equation, $1/\sigma - 1/\sigma_0$ is linear with time. The experimental data in Figure 1 fulfill this requirement.

For the lower temperature data generated at this laboratory (90–150°C), the nylon data did not conform to this relationship. Instead, the data suggested that the degradation initially was inhibited. This assumption seemed reasonable since the yarn contains inhibitors for protection against environmental factors that affect the thermal-oxidative degradation. (Kevlar 29 yarn does not contain inhibitors.) The degradation rate would, therefore, depend on an inhibitor depletion factor:

$$-\frac{d\sigma}{dt} = k_1(\alpha_0 - \alpha)\sigma^2 \quad (2)$$

where α_0 = initial inhibitor concentration and α = inhibitor concentration at time t . Since the decrease in inhibitor concentration and tensile strength are dependent on the same factors, i.e., air and heat, they should also be related and possibly be proportional. There may also be other factors that deplete the

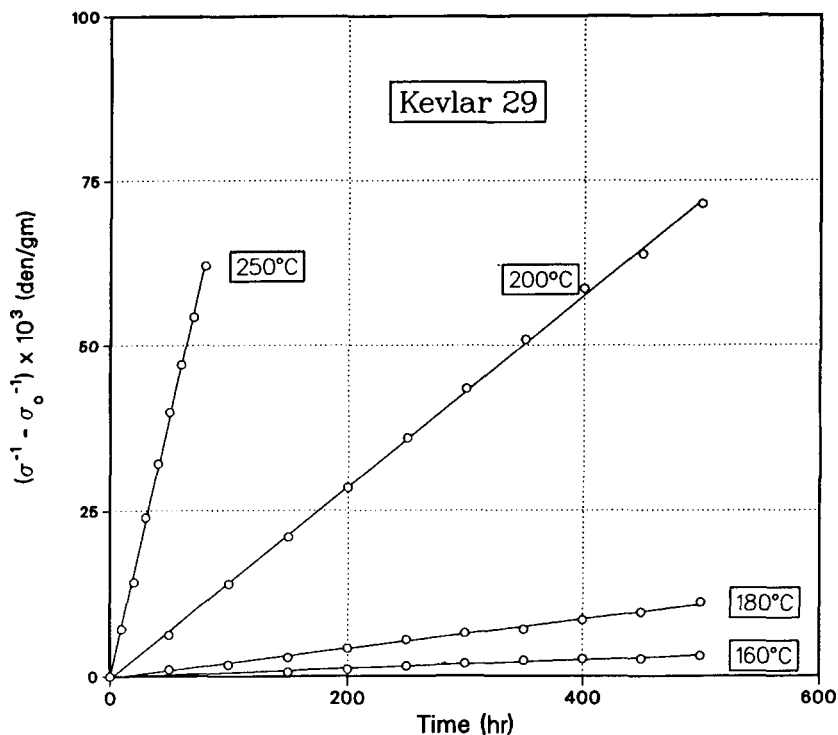


Fig. 1. Du Pont data, second order plot.

inhibitor. A relationship of the following form was therefore assumed:

$$(a_0 - a) = k_2(\sigma_0 - \sigma) + k_3r_3 + k_4r_4 + \dots \quad (3)$$

where k_2, k_3, k_4, \dots are proportionality constants and r_3, r_4, \dots are reactants that deplete the inhibitor and whose concentrations are essentially constant. Substituting into eq. (2) and rearranging this equation gives

$$-\frac{d\sigma}{dt} = k_1k_2\left(\sigma_0 - \sigma + \frac{k_3}{k_2}r_3 + \frac{k_4}{k_2}r_4 + \dots\right)\sigma^2 \quad (4)$$

Letting

$$\alpha = \sigma_0 + \frac{k_3}{k_2}r_3 + \frac{k_4}{k_2}r_4 + \dots \quad (5)$$

and

$$k = k_1k_2$$

reduces eq. (4) to

$$-\frac{d\sigma}{dt} = k(\alpha - \sigma)\sigma^2 \quad (6)$$

Thus, α is a constant larger in value than σ_0 and $(\alpha - \sigma)$ is an inhibitor concentration term, scaled to tensile strength values, which is inversely proportional to the inhibitors that remain. When $t = 0$, the $(\alpha - \sigma)$ value and the degradation rate are at their minima.

Equation (6) modeled the degradation data from this study quite well and permitted the evaluation of α and the rate constants for all temperatures studied. Rate constants were evaluated from the integrated form of eq. (6) given below:

$$kt = \frac{1}{\alpha} \left(\frac{1}{\sigma} - \frac{1}{\sigma_0} \right) + \frac{1}{\alpha^2} \ln \frac{\sigma_0(\alpha - \sigma)}{\sigma(\alpha - \sigma_0)} \tag{7}$$

Effect of Inhibitor

The inhibitor effect became evident when tensile strength vs. time was plotted at several temperatures. Figure 2 is a representative plot for nylon yarn that was exposed to air in 10% humidity at 110, 130, and 150°C. The effect of the inhibitor is most evident at 130°C, where initially the tensile strength degradation rate is minimal, then increases after about 25 days as the inhibitor is being depleted, and finally decreases as the strength approaches zero. An α/σ_0 value of 1.004 provided the best fit for all of the nylon degradation data.

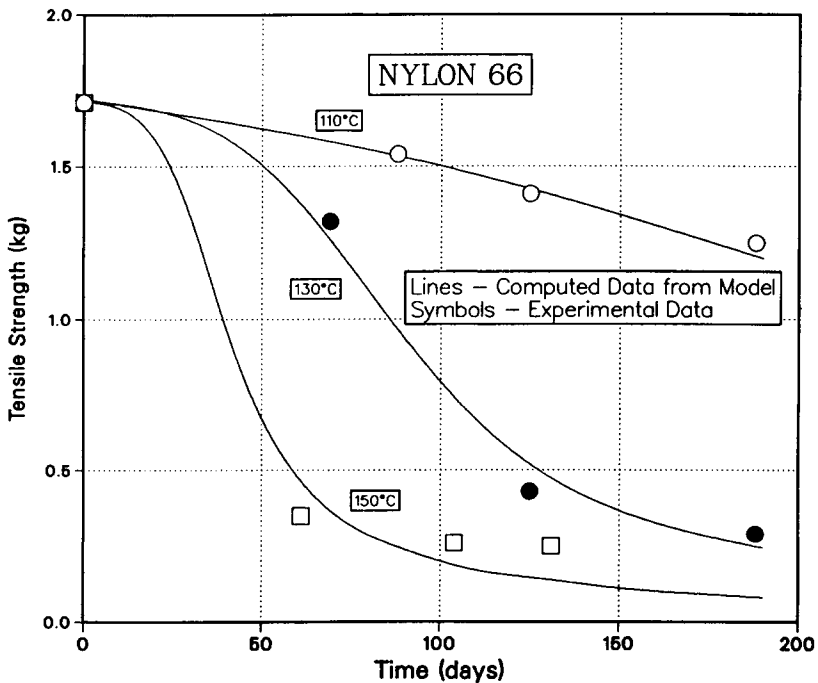


Fig. 2. Tensile strength loss for unknotted nylon in 10% humidity: (—) computed data from model; (○, ●, □) experimental data.

The presence of an induction period in the degradation process (slow initial degradation rate) is common among materials with inhibitors. The study by Mikolajewski, Swallow, and Webb³ shows similar results with nylon 66 fibers (Fig. 3, solid line). Equation (7) modeled these data equally well with an α/σ_0 value of 1.016 (dashed line). Other examples of the induction period for various polymer systems are given in the volume on *Aging and Stabilization of Polymers* by Neiman.⁴

Additional evidence for a second-order degradation model is shown in Figure 4, where three more examples of nylon 66 degradation data are plotted. These data are from the "DuPont Technical Information—Fibers Bulletin."⁵ Two selected examples were those with maximum degradation, 91% (177°C) and 76% (121°C). In these cases, the temperatures were sufficiently high and the inhibitor action sufficiently masked to provide linear plots over the entire time period.

No induction effect due to inhibitors was evident in the DuPont higher temperature Kevlar data (Fig. 1). Insufficient Kevlar data were available from this study at lower temperatures to establish with a reasonable measure of confidence that an inhibitor effect was present. Although eq. (7) modeled these data well, the absence of any known inhibitor in Kevlar negated the possibility that an induction effect would be present. The rate constant values for Kevlar were, therefore, calculated from eq. (1). These values together with those for nylon are tabulated in Table AI of the Appendix.

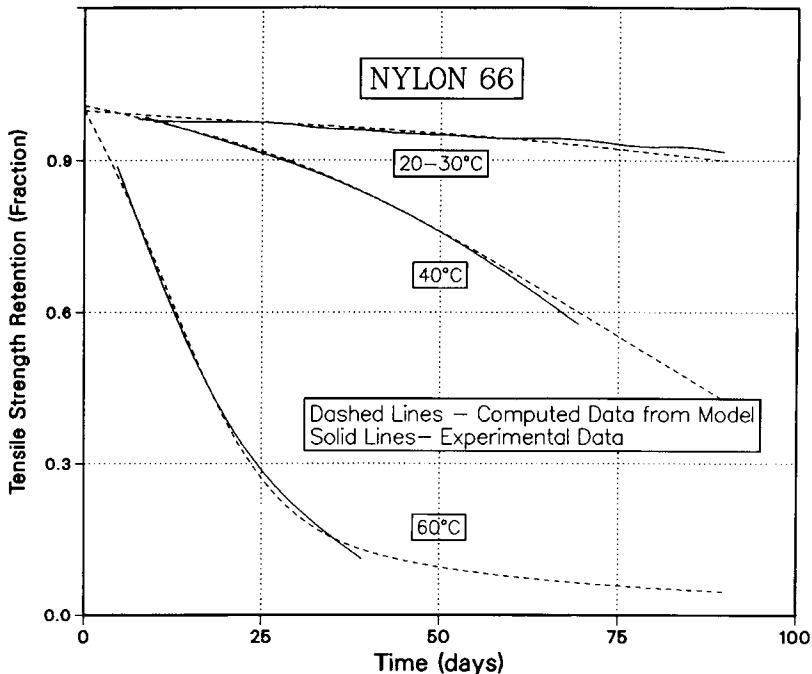


Fig. 3. Correlation of experimental data (—) from Mikolajewski et al.³ with computed data from eq. (7) (---).

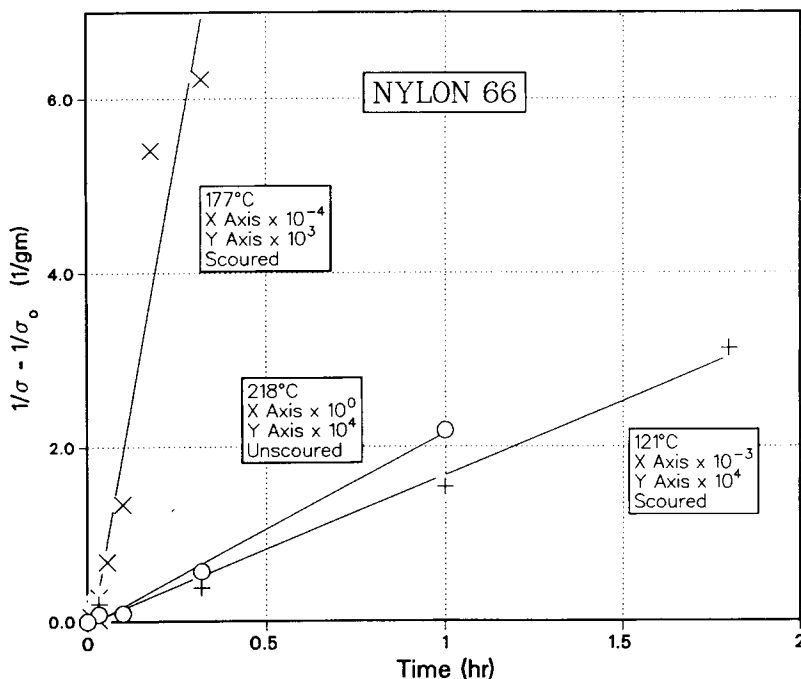


Fig. 4. Representative second order plots from DuPont data.

Effects of Humidity and Temperature

The rate constant values k were found to be sensitive to the moisture environment under the humidity conditions and temperature range of this study. Strength degradation rate constants were obtained in relative humidities of 0–90% measured at ambient conditions. Figure 5 shows the linear relationship between humidity and the rate constants for unknotted nylon and knotted Kevlar yarns obtained at 150 and 170°C, respectively.

The knotted nylon and unknotted Kevlar rate constant data were scattered and did not support the trend indicated in Figure 5. However, the higher values calculated from the 90 and 110°C and 100% RH data (Appendix, Table AII) supported the assumption that moisture increased the degradation rate.

The effect of 100% humidity was measured with containers holding sufficient water in a test tube to assure this condition at the degradation temperature. The appreciably higher rates in this humidity environment necessitated conducting the study at the lower temperatures of 90 and 100°C.

Figure 5 suggested the following relationship:

$$k = k_1 + k_2[\text{H}_2\text{O}] \quad (8)$$

where k_1 and k_2 are the rate constants in the absence and presence of moisture, respectively. Values for k_1 and k_2 were obtained from the slopes and intercepts in Figure 5 and from simultaneous solutions of eq. (8). Values

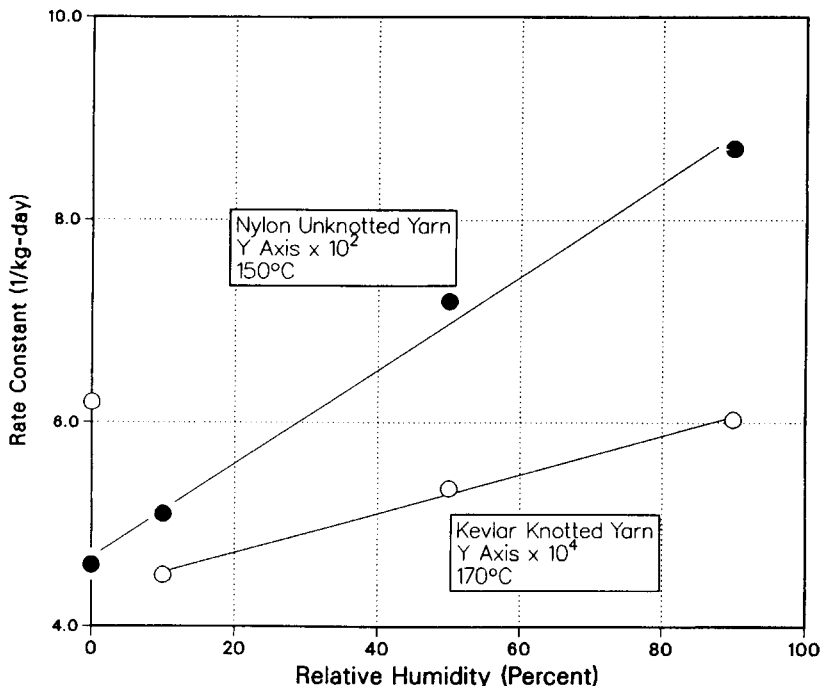


Fig. 5. Effect of humidity on the degradation rate constant.

for k from the 10 and 50% RH conditions obtained at 110, 130, and 150°C were used for these solutions. The values for k at 90 and 100°C and 100% RH for nylon and Kevlar were also used in simultaneous solutions. These values were coupled with 50% RH values for k which were obtained at these lower temperatures from extrapolations of Arrhenius plots (Fig. 6). They are listed in the Appendix, Table AII.

Representative Arrhenius plots for k_1 and k_2 are shown in Figures 7 and 8 for unknotted Kevlar and knotted nylon. Activation energies E and preexponential factors A were evaluated from these plots. They are also listed in the Appendix, Table AIII. Knotted Kevlar provided questionable values.

The above results indicate that two degradation mechanisms are operative, a thermal-oxidative mechanism and one dependent on the presence of moisture. At very high humidities, the moisture-controlled degradation predominates almost to the exclusion of the thermal-oxidative degradation reaction. This conclusion is evident from the ratios of rate constants measured in the presence of air or helium at 100% RH (Table III). These results also show that the moisture-induced reaction requires little if any oxygen. Presumably, the strength loss is due to depolymerization by hydrolysis.

A primary motivation for this study was to obtain estimates for the degradation rate under ambient conditions. Although accelerated aging data are commonly extrapolated to ambient temperatures, incorrect predictions can be obtained if the Arrhenius equation is not applicable. Fortunately, applicability has been established from recent studies performed by Egglestone and George.⁶ They found that accelerated aging test data corre-

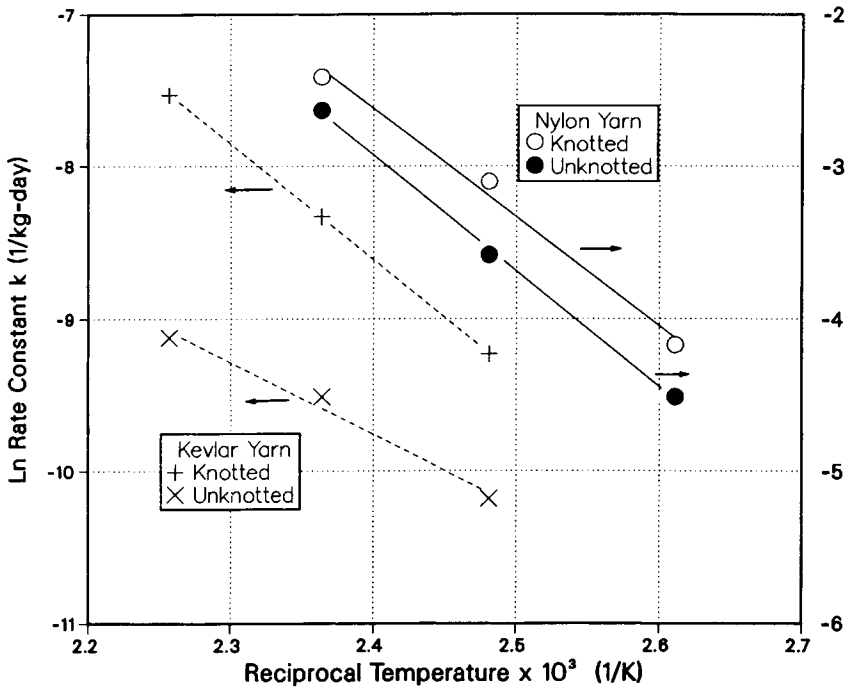


Fig. 6. Effect of temperature on the degradation rate constant. Nylon yarn: (○) knotted; (●) unknotted. Kevlar yarn: (+) knotted; (×) unknotted.

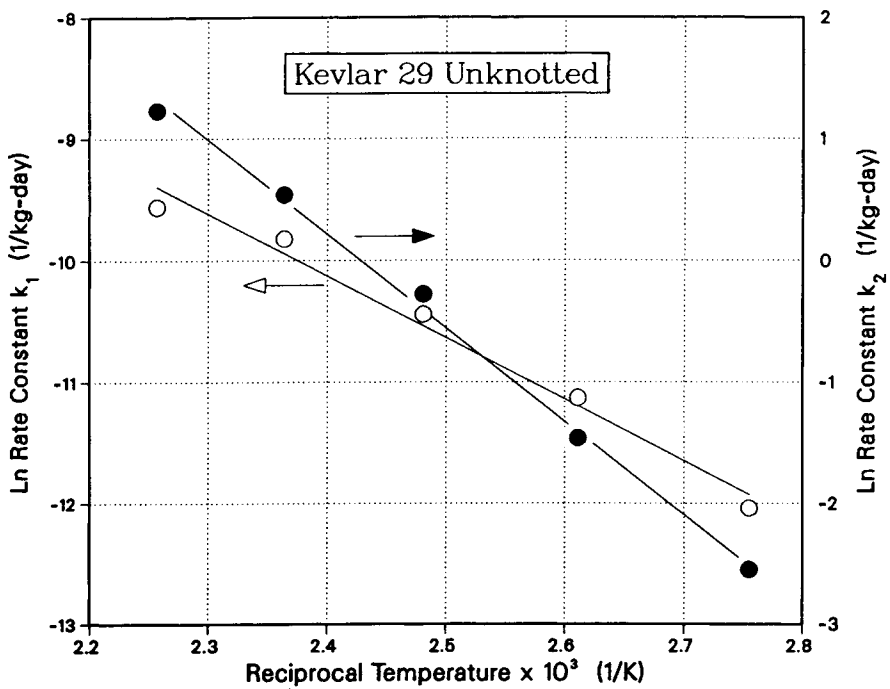


Fig. 7. Effect of temperature on the degradation rate constants k_1 and k_2 .

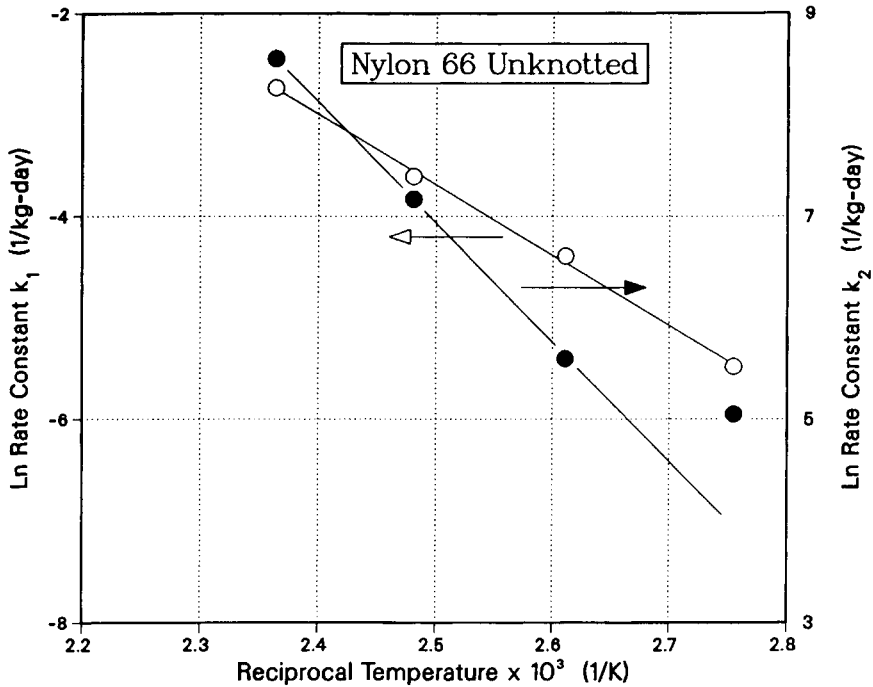


Fig. 8. Effect of temperature on the degradation rate constants k_1 and k_2 .

lated with degradation data obtained from 5- to 20-year-old parachutes whose canopies were made from undyed taffeta and olive drab ripstop nylon 66. For extrapolations of this type, the accuracy of the estimate depends on the precision of the higher temperature data, their range, and the proximity to ambient temperatures. Estimates for the values of the rate constant k at lower temperatures were obtained from eq. (9) below. It utilized kinetic parameter values evaluated from Figures 7 and 8:

$$k = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)[H_2O] \quad (9)$$

The subscripts 1 and 2 refer to the thermal-oxidative and moisture-induced mechanisms, respectively.

Equation (9) reproduced the experimental data reasonably well. Comparative experimental and calculated values are given in the Appendix, Table AI.

TABLE III
Comparative Degradation Rate Constants Measured at 100% Relative Humidity
in the Presence and Absence of Air at 110°C

Yarn	Condition	$k_{\text{air}}/k_{\text{helium}}$
Nylon	Unknotted	1.28
Nylon	Knotted	1.04
Kevlar	Unknotted	.75
Kevlar	Knotted	1.28
		Mean 1.09 ± 0.25

Differences in these values are probably due to the limited experimental data available for evaluating rate constant values and experimental procedures but not tensile strength measurements. The coefficients of variation for the strength measurements were 0.057 and 0.042 for unknotted nylon and Kevlar and 0.144 and 0.155 for knotted nylon and Kevlar, respectively.

Figures 9 and 10 show the effect of three temperatures on degradation over a 25-year period for nylon and Kevlar in 100% RH. The effect of humidity was minimal, being essentially the same at 10% as at 100% RH at 25°C. For the examples cited, the largest difference, 75%, was obtained with nylon at 43°C after 25 years. The differences were smaller at the lower temperatures and less for Kevlar than for nylon.

Two factors contribute to the small effect of humidity on the rate constants at ambient temperatures: (1) The moisture concentrations at 90 and 100°C at 100% RH are factors of 18.4 and 35.9 greater, respectively, than at 25°C, and (2) the activation energies for the moisture-induced degradation components in eq. (9) are factors of 1.6 and 2.0 greater than for the thermal-oxidative degradation components for unknotted Kevlar and both nylons, respectively. Thus the moisture-induced component contributes less to the total degradation at ambient temperatures. The temperature at which the rates for the thermal-oxidative and moisture-induced degradations are equal is 83°C for both unknotted nylon and Kevlar.

Although Kevlar is known to be more stable thermally than nylon, at 25°C nylon appears to degrade less than Kevlar (Figs. 9 and 10). This result is due to the inhibitor action in nylon that in eq. (6) causes the initial degradation

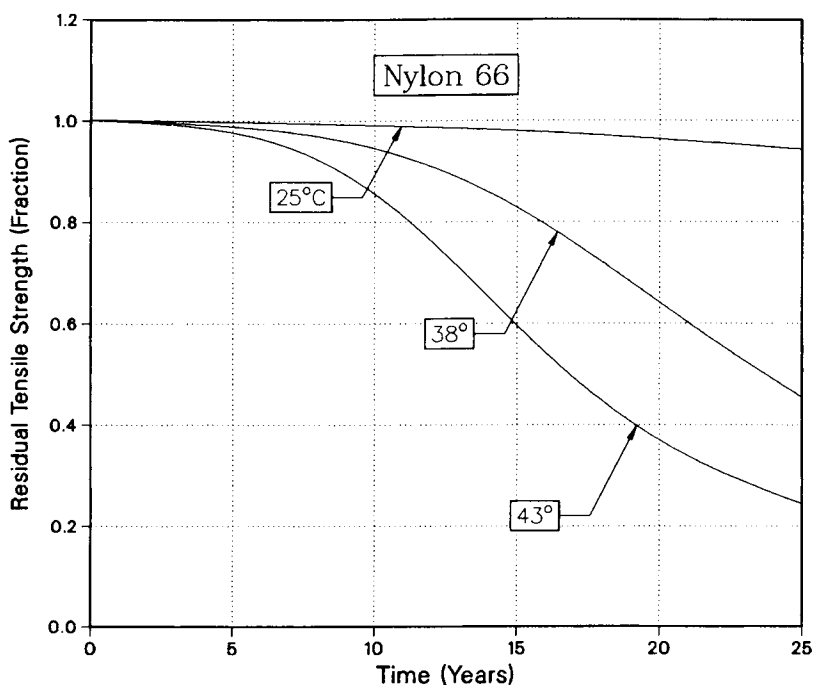


Fig. 9. Tensile strength degradation computed from eq. (7).

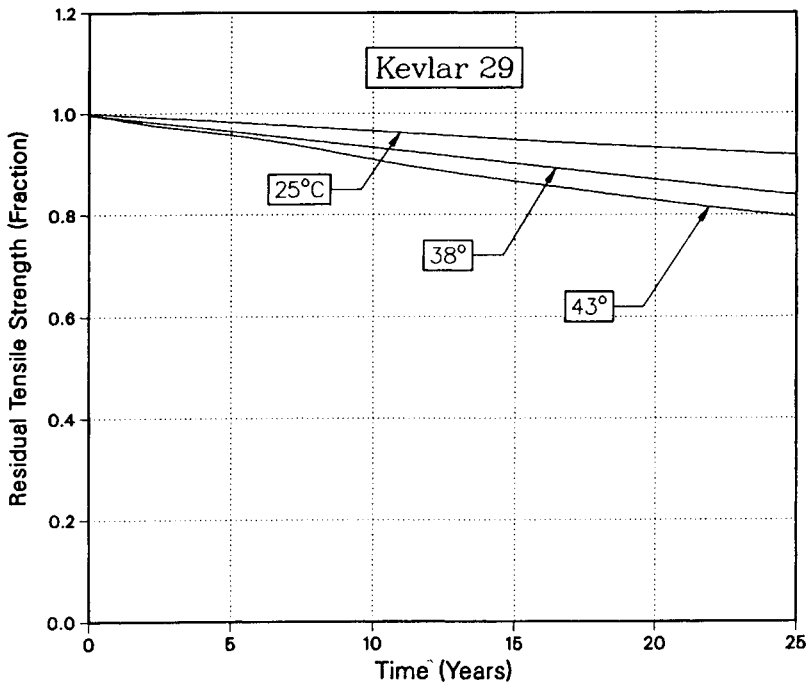


Fig. 10. Tensile strength degradation computed from eq. (1).

rates to be lower than subsequent rates. In contrast, it was assumed that Kevlar does not have an inhibitor. Its degradation rates are provided by eq. (1), which are at their maximum values initially. The greater stability of Kevlar is apparent, however, at the higher temperatures where the inhibitor effect is less pronounced in nylon.

Of primary interest to this study is the apparent result that tensile strength loss is less than 10% at ambient temperatures after 25 years for both nylon and Kevlar. Caveats must be offered with this conclusion, however. Degradation can also depend on environmental factors that are present and on the dye, if any. Thus, Egglestone and George⁶ found that undyed taffeta fabric made for parachute canopies and prepared from nylon 66 degraded 10 times faster than a corresponding olive drab fabric. Auerbach et al.⁷ have found that the blue ink used for identification marking caused nylon ribbons to degrade as much as 75% within three years. Mead et al.¹ have shown that smog will degrade nylon and Kevlar. Although this study provides estimates for the potential useful lifetimes of these yarns, lifetime predictions for fabrics should be confirmed in their application and storage environments.

Effect of Knotting on the Degradation Rates

Half of the specimens in this study were knotted to simulate the tight folding in parachute packs. The plots in Figures 5 and 6 and the rate constant values in the Appendix (Table AI) show that knotting increased the degrada-

TABLE IV
Ratio of Rate Constants for Knotted and Unknotted Yarns

Yarn	Temp (°C)	Atmosphere	RH	Mean ratio k (knotted)/ k (unknotted)
Nylon	25	Air	10-100	1.0
	90	Helium	100	1.4
	110	Helium-Air	100	2.1
	110	Air	10, 50	1.3
	130	Air	10, 50	1.5
	150	Air	0-90	1.6
Kevlar	25	Air	10-100	1.3
	90	Helium	100	24.7
	110	Helium	100	7.8
	110	Air	100	13.3
	130	Air	10, 50	3.4
	150	Air	10, 50	2.9
	170	Air	0-90	4.2

tion rates at the elevated temperatures of this study. The magnitude of this effect is shown in Table IV, where the ratios for unknotted and knotted rate constants are tabulated. The mean ratio value of 1.6 for nylon at elevated temperatures is reduced to 1.0 at 25°C, indicating that the effect of knotting is reduced at lower temperatures. For Kevlar, a mean ratio of 3.5 was obtained at low humidity and elevated temperature conditions but was much higher at 100% RH. At 25°C, the value was reduced to 1.3, indicating again that the effect of knotting is mitigated at ambient temperatures.

CONCLUSIONS

Accelerated aging studies of nylon and Kevlar yarns used in parachutes were conducted over the temperature range of 90-170°C and relative humidities of 0-100%.

At low humidities, a thermal-oxidative mechanism is operative. At very high relative humidities and elevated temperatures, a moisture-induced mechanism predominates. Nylon degradation is inhibited during the early stages and at lower temperatures, presumably because environmental protective agents are present. However, the absence of known inhibitors in Kevlar and the lack of supporting degradation data suggests that Kevlar degradation is not inhibited.

Kinetic models were developed and parameters evaluated. These values permitted 25-year degradation estimates. They show that less than 10% degradation will take place at 25°C for nylon and Kevlar. Although knotted yarns, which simulated tight folding, degraded more rapidly at elevated temperatures, this effect was mitigated at ambient temperatures.

APPENDIX

TABLE AI
 Experimental and Calculated Degradation Rate Constant Values
 for Nylon 66 and Kevlar 29 at Various Relative
 Humidities and Temperatures

Temp. (°C)	Yarn condition	Atmosphere	Humidity (%)	<i>k</i> (1/kg day)	
				Experimental	Calculated
<i>Nylon 66</i>					
90	Unknotted	Helium	100	4.9×10^{-2}	1.2×10^{-2}
110	Unknotted	Helium	100	10.0	9.3
110	Unknotted	Air	100	12.8	9.3
110	Unknotted	Air	10	1.0	1.0
110	Unknotted	Air	50	1.1	1.1
130	Unknotted	Air	10	2.4	2.3
130	Unknotted	Air	50	2.8	2.8
150	Unknotted	Air	0	4.6	4.6
150	Unknotted	Air	10	5.1	5.0
150	Unknotted	Air	50	7.2	6.9
150	Unknotted	Air	90	8.7	8.8
90	Knotted	Helium	100	7.0	2.4
110	Knotted	Helium	100	22.6	23.0
110	Knotted	Air	100	23.5	23.0
110	Knotted	Air	10	1.3	1.3
110	Knotted	Air	50	1.6	1.6
130	Knotted	Air	10	3.3	3.2
130	Knotted	Air	50	4.5	4.3
150	Knotted	Air	0	10.3	6.1
150	Knotted	Air	10	10.0	7.3
150	Knotted	Air	50	9.0	12.3
150	Knotted	Air	90	16.7	17.2
<i>Kevlar 29</i>					
90	Unknotted	Helium	100	3.9×10^{-5}	4.0×10^{-5}
110	Unknotted	Helium	100	20.7	20.9
110	Unknotted	Air	100	15.6	20.9
130	Unknotted	Air	10	3.1	2.9
130	Unknotted	Air	50	3.8	3.5
150	Unknotted	Air	10	5.8	5.3
150	Unknotted	Air	50	7.4	6.8
170	Unknotted	Air	0	15.3	8.5
170	Unknotted	Air	10	11.5	9.4
170	Unknotted	Air	50	11.0	12.7
170	Unknotted	Air	90	14.2	16.0
90	Knotted	Helium	100	96.	63.
110	Knotted	Helium	100	162.	210.
110	Knotted	Air	100	207.	210.
130	Knotted	Air	10	8.9	7.3
130	Knotted	Air	50	9.8	11.1
150	Knotted	Air	10	14.	15.8
150	Knotted	Air	50	24.	17.3
170	Knotted	Air	0	61.	30.3
170	Knotted	Air	10	45.	32.4
170	Knotted	Air	50	53.	41.1
170	Knotted	Air	90	60.	50.0

TABLE AII
 Rate Constant Values for k_1 and k_2

Yarn	Yarn condition	Temperature (°C)	k_1	k_2
			(1/kg day)	(1/kg day)
Nylon 66	Unknotted	90 ^a	0.0024	110
	Unknotted	110	0.0098	108
	Unknotted	130	0.0230	434
	Unknotted	150	0.0461	2098
	Knotted	90 ^a	0.0042	155
	Knotted	110	0.0124	271
	Knotted	130	0.0270	1300
	Knotted	150	0.0643	5154
Kevlar 29	Unknotted	90 ^a	0.589×10^{-5}	0.0782
	Unknotted	110 ^a	1.40	0.233
	Unknotted	110	1.47	0.171
	Unknotted	130	2.93	0.760
	Unknotted	150	5.41	1.72
	Unknotted	170	7.00	3.47
	Knotted	90 ^a	1.48×10^{-5}	2.30
	Knotted	110 ^a	1.30	1.94
	Knotted	110	0.666	2.50
	Knotted	130	8.82	0.499
	Knotted	150	11.9	10.5
	Knotted	170	44.0	8.24

^aHelium environment.

 TABLE AIII
 Arrhenius Kinetic Parameter Values

Yarn	Condition	A_1	A_2	E_1	E_2
		(1/kg day)		(kcal/mol)	
Nylon 66	Unknotted	8.61×10^4	6.37×10^{15}	12.1	24.1
	Knotted	2.34×10^5	1.90×10^{16}	12.7	24.2
Kevlar 29	Unknotted	7.63	1.36×10^8	10.0	15.3
	Knotted	2059	4.19×10^4	13.8	7.37

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