



AD-A156 909

DEPARTMENT OF DEFENCE
DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
MATERIALS RESEARCH LABORATORIES
MELBOURNE, VICTORIA

REPORT

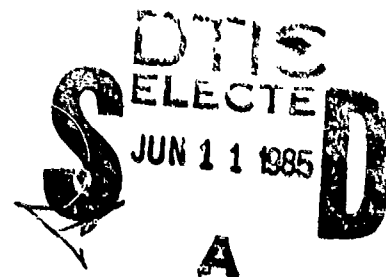
MRL-R-950

AGE-LIFE PREDICTION OF NYLON 66 PARACHUTE
MATERIALS - PART 2. CHANGES IN THE CHEMICAL AND PHYSICAL
PROPERTIES OF MATERIALS ON AGING

G.T. Egglestone and G.A. George

DTIC FILE COPY

Approved for Public Release



JANUARY, 1985

~~85-03-10-041~~

**DEPARTMENT OF DEFENCE
MATERIALS RESEARCH LABORATORIES**

**REPORT
MRL-R-950**

**AGE-LIFE PREDICTION OF NYLON 66 PARACHUTE
MATERIALS - PART 2. CHANGES IN THE CHEMICAL AND PHYSICAL
PROPERTIES OF MATERIALS ON AGING**

G. Egglestone and G.A. George

ABSTRACT

Changes in the chemical properties of nylon 66 taffeta material and olive drab ripstop material on accelerated thermal aging are reported. The thermooxidative changes that occurred were used to measure rates and degree of polymer degradation. Relationships between tensile strength, molecular weight and other chemical changes were established and found to be applicable for in-service parachutes.

The nylon 66 materials were also examined for photochemical degradation after outdoor exposure. No phototendering was found for the dyed material and the difference in degradation rates was attributed to different stabilizers being used during fibre manufacture. *This is an Australian Department of Defence document.*

Approved for Public Release

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

DOCUMENT CONTROL DATA SHEET

REPORT NO.
MRI-R-950AR NO.
AR-004-199REPORT SECURITY CLASSIFICATION
Unclassified

TITLE

Age-life prediction of nylon 66 parachute materials - Part 2.
Changes in the chemical and physical properties of materials on aging

AUTHOR(S)

G.T. Egglostone and G.A. George

CORPORATE AUTHOR

Materials Research Laboratories
P.O. Box 50,
Ascot Vale, Victoria 3032

REPORT DATE
January, 1985TASK NO.
ARM 81/038SPONSOR
ArmyCLASSIFICATION/LIMITATION REVIEW DATE
January, 1988CLASSIFICATION/RELEASE AUTHORITY
Superintendent, MRI
Organic Chemistry Division

SECONDARY DISTRIBUTION

Approved for Public Release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Nylon 66
Degradation
Parachutes

Polyamide
Thermal analysis
Chemical viscosity
Solar radiation
Outdoor exposure

COSATI GROUPS 1111

ABSTRACT

Changes in the chemical properties of nylon 66 taffeta material and olive drab ripstop material on accelerated thermal aging are reported. The thermooxidative changes that occurred were used to measure rates and degree of polymer degradation. Relationships between tensile strength, molecular weight and other chemical changes were established and found to be applicable for in-service parachutes.

The nylon 66 materials were also examined for photochemical degradation after outdoor exposure. No phototendering was found for the dyed material and the difference in degradation rates was attributed to different stabilizers being used during fibre manufacture.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

C O N T E N T S

Page No.

1.	INTRODUCTION	1
2.	EXPERIMENTAL	2
	2.1 Dynamic Mechanical Measurements	2
	2.2 Molecular Weight Measurements	2
	2.3 Chemical Analysis	2
	2.3.1 Carbonyl Groups	2
	2.3.2 Amine and Carboxylic Acid End Groups	2
	2.4 Dye Analysis and Phototendering Experiments	3
3.	RESULTS AND DISCUSSION	3
	3.1 Molecular Weight Changes during Thermal Aging	3
	3.2 Amine End Groups	4
	3.3 Carbonyl and Carboxyl Groups	5
	3.4 Relation Between Retained Strength and Chain Scissions Measured by Carboxyl Group Concentration	6
	3.5 Degradation during Outdoor Exposure	7
4.	CONCLUSIONS	8
5.	REFERENCES	9

Accession For

NTIS GRA&I ☒

DTIC TAB ☐

Unannounced

Justification

By _____

Distribution/

Availability Codes

Avail and/or

Special

Dist **A1**



AGE-LIFE PREDICTION OF NYLON 66 PARACHUTE
MATERIALS - PART 2. CHANGES IN THE CHEMICAL AND PHYSICAL
PROPERTIES OF MATERIALS ON AGING

1. INTRODUCTION

Nylon 66 parachute materials have been found to undergo a progressive loss of strength during storage and service. In studies detailed in Part 1 of this report [1] it was found that significant losses of strength occurred in unused parachutes in storage. Accelerated thermal aging studies on parachute canopy material at temperatures from 65°C to 110°C were used to determine an extrapolated rate of degradation at storage temperatures. These results gave good agreement with measured strength losses from parachutes stored for up to 20 years and accelerated aging data were used for predicting the service life of a new nylon 66 ripstop material [1] used in the manufacture of the present range of T-10 personnel parachutes. Results showing the performance of the canopy materials when exposed to sunlight were also presented in Part 1 of this report.

These results did not provide any insight into the reasons for the slow strength losses occurring on storage or the relative rates of strength loss from the two types of canopy material studied by accelerated thermal aging and outdoor exposure. In this report a study of the physical and chemical changes occurring in the materials during degradation is reported. These results are interpreted within the framework of the known chemical reactions occurring in nylon 66 polymers during thermal and photochemical oxidation. From these studies the processes of strength losses occurring on aging can be rationalised.

2. EXPERIMENTAL

The materials studied in this report were identical to those used for mechanical measurements in Part 1. The material consisted of fabric woven from yarns of oriented nylon 66 fibres of average diameter 20 μm . The polymer was confirmed to be poly(hexamethylene adipamide) by Differential Thermal Analysis. The following polymer property and chemical analysis measurements were performed.

2.1 Dynamic Mechanical Measurements

The glass transition temperature T_g was determined using a Rheovibron DDV-11-C Dynamic Viscoelastometer operated at a constant frequency of 110 Hz. The sample grips were modified as described by Massa et al [2] to minimize slippage of the 5 mm strips of fabric. The temperature was monitored using a chromel alumel thermocouple held near the sample surface. T_g is defined as the temperature at which the loss factor, $\tan \delta$, is a maximum.

2.2 Molecular Weight Measurement

Nylon 66 fibres were dissolved in m-cresol, centrifuged to remove any pigments, and the intrinsic viscosity $[\eta]$ measured at 25°C with an Ubbelohde dilution viscometer. The viscosity average molecular weight, M_v , was obtained by using the constants $K = 240 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.61$ in the Mark-Houwink Equation [3].

$$[\eta] = k M_v^a$$

2.3 Chemical Analysis

2.3.1 Carbonyl Groups

The concentration of aldehyde and keto acidic groups in the nylon fibres were determined by their reaction with 2-methoxyphenol in concentrated sulphuric acid [4]. This reaction gives a red coloration due to a complex with a carbonyl group, and the concentration may be determined from the extinction coefficient of $12,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 530 nm.

2.3.2 Amine and Carboxylic Acid End Groups

Amine end groups on the nylon were determined by conductometric titration of a nylon solution in phenol using 0.01 M hydrochloric acid [5]. Acid end groups were determined by titration of a 0.2 g sample of nylon dissolved in benzyl alcohol at 185°C with a 0.01 M solution of potassium hydroxide in benzyl alcohol, to a phenolphthalein end point. A blank determination compensated for the carboxyl groups formed by heating benzyl alcohol in air [5].

2.4 Dye Analysis and Phototendering Experiments

In Part 1 of this report it was noted that nylon ripstop material dyed olive drab showed a much greater rate of strength loss than the plain white taffeta material when exposed outdoors [1]. As it is known that certain dyes can increase the rate of photo-degradation of nylon 66 [6] (phototendering) the dyes used in this material were examined. The olive drab material was extracted with pyridine to remove the dyestuff. This was then separated by high performance liquid chromatography into three component dyes coloured light blue, dark blue and orange.

To determine if any of these dyes were responsible for phototendering, these three colours plus the original olive drab were applied to nylon yarns using a conventional dyeing system. Acetic acid was added towards the end of the dyeing cycle to aid exhaustion.

These samples, together with undyed yarns, were mounted outdoors at MRI, at an angle of 36° to the horizontal and the mechanical properties measured periodically. The solar radiation dose was measured by changes in absorbance at 340 nm of poly(phenylene oxide) films [7].

3. RESULTS AND DISCUSSION

3.1 Molecular Weight Changes during Thermal Aging

The loss of strength of the nylon 66 polymer that occurs on thermal aging can result from either:

- (i) a decrease in the energy to fracture the polymer because of crystallization;
- (ii) a decrease in the molecular weight of the polymer due to chain scission reactions.

The dynamic mechanical measurements of nylon 66 during thermal aging show that there is little change in the breadth or height of the loss peak, both of which would be expected to change if the crystallinity altered [8].

There is, however, a decrease in viscosity average molecular weight as shown in Figure 1 for thermal aging of both nylon 66 taffeta and ripstop materials at 110°C . While the data show substantial scatter, there is a clear trend for a decrease in M_v with time of aging and the loss in strength is attributed to scission of the polymer chain. It is possible that some chain crosslinking also occurs. This could be detected by measurement of the complete molecular weight distribution of the polymer. The change in M_v in both types of materials is accompanied by a significant change in the chemical composition of the polymer.

Nylon 66, as manufactured, contains both terminal acid and amine groups. These end groups can be analysed by the methods in Section 2.3.2 to give the number average molecular weight ($\bar{M}_n$) of the polymer. It was found that, during accelerated thermal aging of the nylon 66 taffeta material, there were changes in the concentrations of these end groups.

3.2 Amine End Groups

There was a rapid decrease in the amine group concentration with time of exposure at elevated temperature. This is shown in Figure 2 for temperatures of 65°C, 80°C, 100°C and 110°C.

These experiments show that the nylon 66 fibre samples reach a final amine end group concentration, C_∞ , of about $22 \mu\text{mol g}^{-1}$ after prolonged thermal aging, independent of the temperature. The disappearance of amine end groups was tested for being first order in amine concentration, C , by plotting $\log [C - C_\infty / C_0 - C_\infty]$ against time of aging. C_0 is the original concentration of amine end groups in the fibre ($61 \mu\text{mol/g}$). A plot of the data for amine end group disappearance at 80°C and 100°C is given in Figure 3 and it can be seen that first order kinetics are obeyed. Table 1 summarises the rate constants for amine disappearance at the test temperatures. Figure 4 shows that these data fit an Arrhenius relation over this temperature range giving a pre-exponential factor A of $2.2 \times 10^8 \text{ s}^{-1}$ and an activation energy, E_a , of 71.0 kJ mol^{-1} . This value for the activation energy is significantly lower than the value of $151.2 \text{ kJ mol}^{-1}$ reported by Valko and Chiklis over the temperature range 136°C to 192°C [9]. It is noted that the temperatures in their study are above the glass transition temperature of 107°C of the nylon 66 fibre measured in this investigation by dynamic mechanical methods. It has been reported that the rate of many polymer reactions such as oxidation increases above the glass transition temperature [10] and it is not expected that the mechanism for amine consumption at the high temperatures studied by Valko and Chiklis would necessarily be the same as that at lower temperatures.

It is of interest to note the significance of the value of C_∞ , the concentration of amine end groups that cannot undergo chemical reaction. The value of $22 \mu\text{mol g}^{-1}$ represents 36.1% of the original concentration, C_0 . A typical nylon 66 fibre has a degree of crystallinity ranging from 36 to 41% so it is reasonable to assume that C_∞ represents those amine end groups that lie in the crystalline region. This explains the lack of reactivity of these end groups as only the chains in amorphous regions have sufficient mobility to undergo chemical reaction.

Among the possible reasons for the disappearance of amine end groups during thermal aging, further polycondensation with terminal carboxyl groups and free-radical oxidation would appear the most likely. The process of thermal aging leads to an immediate and rapid increase in the carboxyl group concentration and there is also a decrease in the molecular weight of the polymer. These results favour the process of oxidation rather than further polycondensation as will be argued below.

3.3 Carbonyl and Carboxyl Groups

There is a significant change in the extent of oxidation of the polymer on aging. In Table 2 the changes of carbonyl and carboxyl group concentration in the polymer with time of aging at 110°C are compared.

The changes in carboxyl group concentration with time of aging at temperatures of 65°C, 80°C, 100°C and 110°C, are shown in Figure 5. The rapid increase in carboxyl as well as carbonyl group concentration clearly indicates that the chemical changes occurring on thermal aging are due to oxidation of the polymer. The rate of formation of carbonyl groups is much lower than carboxyl groups. At 110°C the initial rates of formation are respectively $0.275 \mu\text{mol g}^{-1} \text{ day}^{-1}$ and $2.7 \mu\text{mol g}^{-1} \text{ day}^{-1}$.

The growth of carboxyl groups at temperatures of 65°C and 80°C appears to be linear with time. However, at 100°C and 110°C the curves indicate that carboxyl group formation follows first order kinetics. This is tested in Figure 6 and it is seen that the data at 110°C fits the relation

$$[\text{COOH}]_0 = [\text{COOH}]_{\infty} (1 - e^{-k_1' t})$$

where

$$[\text{COOH}]_{\infty} = 103 \mu\text{mol g}^{-1}$$

$$k_1' = 0.025 \text{ day}^{-1}$$

$$[\text{COOH}]_0 = (\text{carboxyl concentration at time 't' - carboxyl concentration at time 'to'})$$

$$[\text{COOH}]_{\infty} = (\text{maximum concentration of carboxyl - carboxyl concentration at time 'to'})$$

where k_1' is the rate constant for carboxyl groups formation by the overall reaction (1), which consists of many separate reactions (11).



$$\text{i.e.} \quad -\frac{d[\text{RH}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{d[\text{R'COOH}]}{dt} = k_1' [\text{RH}] [\text{O}_2]$$

At high oxygen partial pressures the concentration of oxygen is not rate determining.

It is noted that while carbonyl oxidation products may result either from oxidation of the chain without chain scission or by a radical reaction such as β scission (11), carboxyl group formation can occur only as a result of chain scission since nylon 66 is an unbranched condensation polymer. Thus

all carboxyl groups are at chain ends, and the increase in carboxyl group concentration monitors the decrease in molecular weight of the polymer due to polymer chain scissions.

Since each carboxyl group per molecular corresponds to a maximum of one chain scission, then a measure of the chain scissions will be given by

$$S' = \frac{[\text{COOH}]}{[\text{COOH}]_{\text{to}}} - 1$$

This chemical method for measuring degradation can be compared with the physical measurement of chain scissions, S , from the decrease in molecular weight.

where:

$$S = \frac{\bar{M}_v}{\bar{M}_{v0}} - 1$$

This is shown in Table 3 for aging at 110°C. A plot of S against S' (Figure 7) shows that the chemical method indicates a higher number of chain scissions at short times of aging than is determined from $\bar{M}_v$. Whether this indicates substantial crosslinking (perhaps through the amine end groups) is uncertain. A broadening of the molecular weight distribution with little change in $\bar{M}_v$ could occur. Determination of the molecular weight distribution by size exclusion chromatography would be required to elucidate this further. The rate of polymer chain scissions at long aging times can be determined from the molecular weight data of Figure 1.

3.4 Relation between retained strength and chain scissions measured by carboxyl group concentration

From the temperature dependence of the rate of formation of carboxyl group formation (Table 4) the activation energy for polymer chain scissions may be determined. This is shown in Figure 8, and gives an activation energy of 58 kJ/mol which is only slightly lower than the value of 66.5 kJ/mol for the activation energy calculated for the rate of loss of strength of nylon 66 taffeta (1). As the loss of strength on aging results from the scission of the polymer chain, there should be a simple relation between S' , as measured from carboxyl group concentration, and the loss in strength of the material. This follows since, in many polymers, the relationship between strength σ , and number average molecular weight $\bar{M}_n$ is given by (12)

$$\sigma = A - \frac{B}{\bar{M}_n} \quad \text{where } A \text{ and } B \text{ are constants}$$

If $\Delta\sigma$ is the loss in strength, then

$$\begin{aligned}\Delta\sigma &= \sigma_0 - \sigma = S\left(\frac{1}{\bar{M}_n} - \frac{1}{\bar{M}_n^0}\right) \\ &= \frac{RS'}{\bar{M}_n^0} \\ &= \text{const. } S'\end{aligned}$$

This relationship is shown in Figure 9 using accelerated aging data at 80°C. This can be tested by using Figure 9 to determine the expected strength loss from an actual parachute in which the carboxyl concentration has been determined. The change in carboxyl group concentration with the age of the parachute canopy material is shown in Figure 10. At 15 years the calculated chain scission S' from Figure 10 are 0.7 per molecule. From Figure 9 this predicts a strength loss of 19.2%. The measured loss in tensile strength of the material is 19% (Figure 6, Part 1).

In a recent report [12] the change in the chemical composition of thermally aged nylon 66 yarn has been measured by UV-visible absorption spectrophotometry and related to the loss in tensile strength. While the chemical species responsible for the change in UV absorption was not identified, this report demonstrated the sensitivity of a chemical method for determining the degree of tensile strength loss in aged yarns. The results reported here also demonstrate that the chemical changes in carboxyl concentration of the fibre can be used to predict strength losses from nylon parachute materials held in storage. In addition, accelerated aging methods may be used to duplicate the changes occurring on long term storage provided that the test temperatures do not largely exceed the glass transition temperature of the nylon 66 fibre (107°C).

1.5 Degradation during Outdoor Exposure

As detailed in Part 1, the olive drab ripstop and undyed taffeta materials both showed a decrease in strength on outdoor exposure, but it was found that the dyed ripstop degraded faster. This is opposite to the behaviour in thermal aging [1].

Molecular weight measurements on both materials confirmed that the olive drab material showed a faster rate of chain scission than the undyed taffeta. These results are summarised in Table 5. Once again polymer chain scissions (in this case calculated from molecular weight data) are simply related to the loss in strength as shown in Figure 11 for both types of material.

The possibility of the difference in the rates of photochemical degradation arising from sensitisation of the nylon ripstop by one of the components of the olive drab dye has been investigated. As shown in Figure 12, there is a systematic increase in the reflectance of the nylon 66 material

at 400 nm with solar radiation dose. This could result from photodegradation of one of the dyestuffs that leads to fading on outdoor exposure [13]. Whether this reaction contributes to an increased rate of photo-oxidation of the nylon substrate is uncertain, and the following experiments were performed to examine the phototendering effect of any of the dye components.

As detailed in the experimental section, the component dyes were separated from the olive drab material, applied to nylon 66 yarns and exposed outdoors. The tensile strength of the yarns was measured as a function of solar dose. The results are summarised in Table 6 and it can be seen that, within the expected scatter of mechanical measurements, none of the component dyes produced an increase in the rate of tensile strength loss compared to the undyed yarn. Of particular interest is the observation that the orange dye shows a photostabilising effect. As a detailed chemical analysis of the dye components has not been performed no further conclusions can be drawn. It does not appear from these experiments that the dyes are responsible for the increased rate of degradation of the ripstop material.

The differences between the materials therefore must arise from differences in the stabilizers in the nylon 66 fibres, yet extraction and HPLC analysis has so far failed to reveal significant differences.

4. CONCLUSIONS

It was shown that the thermo-oxidative processes occurring during aging of nylon 66 can be used to monitor the rates and degree of polymer degradation. These rates can be determined by changes in the polymer carbonyl, carboxyl and amine concentrations, as well as the more conventional molecular weight measurements.

The formation of carboxyl end groups was found to occur via a first order reaction, with the initial rate of formation at a temperature near T_g of the polymer being 10 times that for carbonyl formation. This indicated that the oxidation reaction was complete and few end of chain carbonyls existed. The carboxyl groups which only occur at chain ends were used as a measure of the number of chain scissions occurring. A correlation between chain scissions and tensile strength loss was found. This was tested and the results showed it to be applicable for in-service parachutes.

Rates for photochemical degradation were also determined. Although parachutes are expected to see very little sunlight, some dyestuffs are known to accelerate the rate of degradation through phototendering. The rate of photodegradation was faster for the olive drab dyed material than for the undyed material. Subsequent exposure trials using the olive drab dye mixture and the individual dye components showed no phototendering effects. More likely the differences in rates result from different UV stabilizers being used. The results obtained for the photodegradation are opposite to those for thermal oxidation, where the undyed nylon 66 was shown to degrade faster than the olive drab dyed nylon 66 [1].

5. REFERENCES

1. Egglestone, G.T. and George, G.A. 'Age Life Prediction of Nylon 66 Parachute Materials' Part-1. Mechanical Properties, Report MRL-R-930, 1984.
2. Massa, D.J., Flick, J.R. and Petrie, S.E.B. (1975). ACS Coat. Plast. Prepr., 35, 371.
3. Burke, J.J. and Orofino, T.A. (1969). J. Polym. Sci. A-2, 7, 1.
4. Schmitz, F.P. and Muller, H. (1979). Kunststoffe, 69, 321.
5. Waltz, J.E. and Taylor, G.B. (1947). Anal. Chem., 19, 448.
6. Allen, N.S. and McKellar, J.F. (1980). Chapter 7 in 'Developments in Polymer Photochemistry - 1'. Ed. N.S. Allen, Applied Science (London).
7. Davis, A., Gordon, D. and Howell, G.V. 'Continuous World Wide UV Monitoring Program', Report ERDE TR-141, 1973,
8. Murayama, T. (1978). 'Dynamic Mechanical Analysis of Polymeric Material', p.75. Elsevier (Amsterdam).
9. Valko, E.I. and Chiklis, C.K. (1965). J. Appl. Polym. Sci. 9, 2855.
10. Garton, A., Carlsson, D.J. and Wiles, D.M. (1980). Chapter 4 in 'Developments in Polymer Photochemistry - 1'. Ed. N.S. Allen, Applied Science (London).
11. Mayo, F.R. (1970). National Bureau of Standards Special Technical Publication 357, 95.
12. Billmeyer, F.W. (1971). 'Textbook of Polymer Science', p.233, 2nd Edition, Wiley-Interscience (N.Y.).
13. Renschler, C.S. and Burns, F.B., (1984). J. Appl. Polym. Sci., 29, 1125.
14. Horsfall, G.A. (1982). Text. Res. J. 52, 197.

T A B L E 1

Rate Constants for Disappearance of Amine End Groups

T°C	k (day ⁻¹)
110	0.0450
100	0.0393
80	0.0063
65	0.0029

T A B L E 2

Concentration of Carbonyl and Carboxyl Groups

in Nylon Taffeta Aged at 110°C

Days aged	Carbonyl Concentration (mol/g)	[COOH] Carboxyl Concentration (mol/g)	$\frac{[\text{Carbonyl}]}{[\text{COOH}]}$
0	0.2×10^{-6}	64×10^{-6}	3.0×10^{-3}
2	0.8×10^{-6}	75×10^{-6}	1.0×10^{-2}
3	0.6×10^{-6}	76×10^{-6}	7.9×10^{-3}
32	2.14×10^{-6}	105×10^{-6}	2.0×10^{-2}

T A B L E 3

Comparison of Number of Polymer Chain Scissions, S, Calculated from $\bar{M}_v$
with those Calculated from Carboxyl Group Concentration, S'.

Data for Nylon 66 Undyed Taffeta Aged at 110°C

Time of Aging	[COOH]	S'	S
0	64	0	0
1	68	0.06	0.04
2	75	0.17	0.2
3	76	0.19	0
7	81	0.26	0.06
21	97	0.52	0.32
32	105	0.64	0.46
49	127	0.98	0.87
75	148	1.31	1.38

TABLE 4

Temperature Dependence of the Rate of Chain Scission Calculated
from Carboxyl Group Concentration for Nylon Taffeta

T°C	ds'/dt (scissions day ⁻¹)
65	0.0014
80	0.0040
100	0.0067
110	0.0163

TABLE 5

Viscosity Average Molecular Weight of Canopy

Materials Exposed Outdoors

Days Exposed	Total Dose GJ/m ²	Molecular Weight $\bar{M}_v$	
		Olive Drab Material	Undyed Taffeta Material
0	0	23,300	22,850
17	0.18	21,650	19,350
38	0.46	18,500	19,650
59	0.80	18,650	19,250
111	1.89	14,650	17,100
131	2.35	10,000	16,300
181	3.44	8,700	8,050

TABLE 6

Tensile Strength and Energy to Fracture Measurements for
Redyed Nylon Yarns Exposed Outdoors

Days exposed	Total Dose GJ/m ²	Percentage Tensile Strength Loss				
		Undyed Yarn	Olive Drab	Orange	Dark Blue	Light Blue
14	0.12	0.9	3.6	0.6	4.8	2.4
34	0.34	5.7	12.5	4.2	4.5	8.3
86	1.21	23.8	24.1	19.3	24.1	21.1
108	1.68	33.9	29.4	17.5	30.6	30.3

Days aged	Total Dose GJ/m ²	Energy to Fracture at Break (Joule)				
		Undyed Yarn	Olive Drab	Orange	Dark Blue	Light Blue
14	0.12	-	-	6.35	6.38	5.79
34	0.34	4.43	5.73	6.58	5.49	5.29
86	1.21	2.89	4.12	4.01	3.84	4.31
108	1.68	2.12	3.60	4.44	3.18	3.45

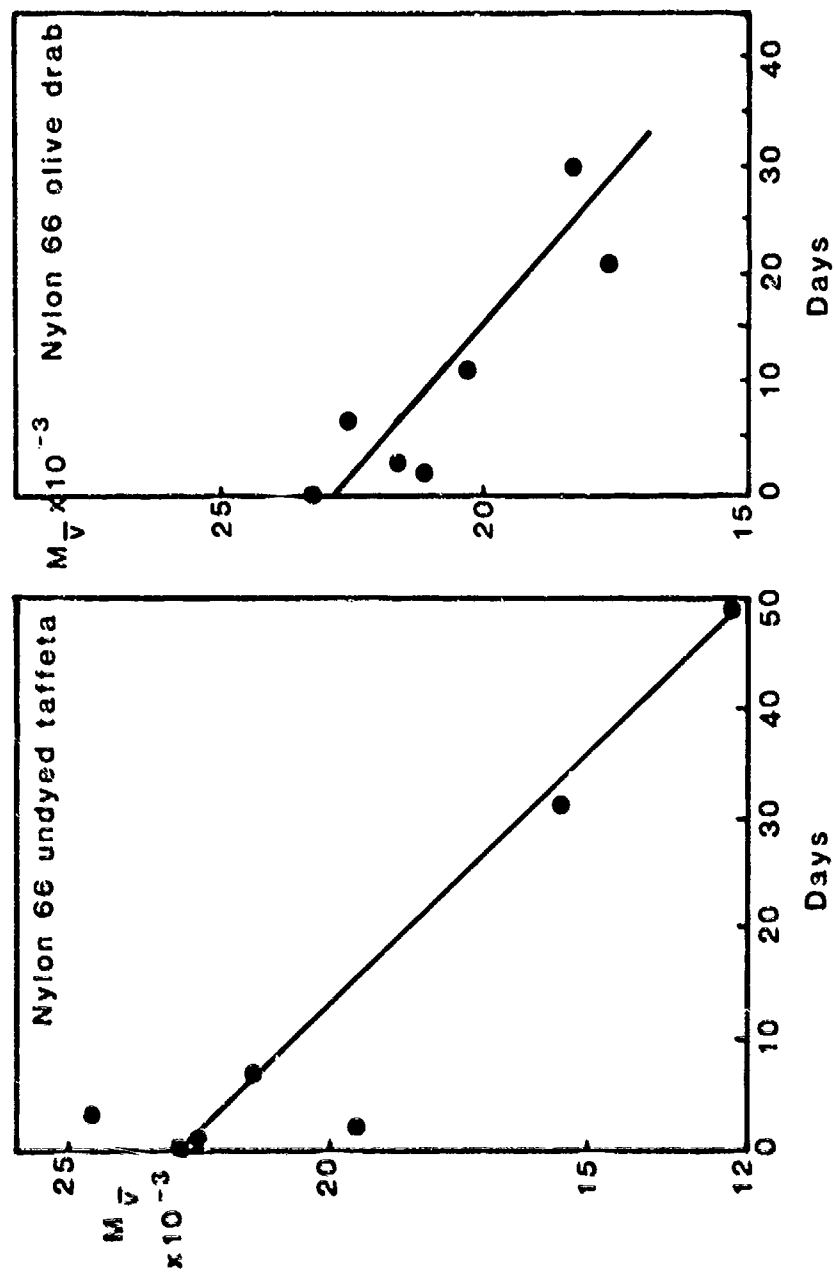


FIGURE 1 Changes in viscosity average molecular weight ($\bar{M}_v$) with time of aging at 110°C.



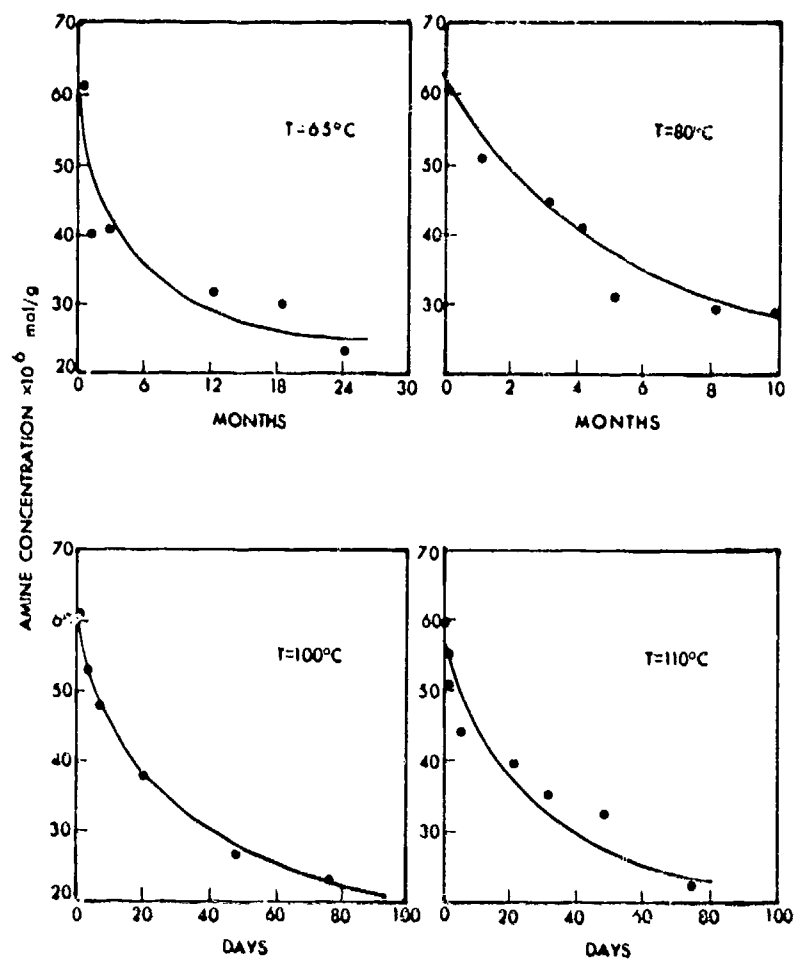
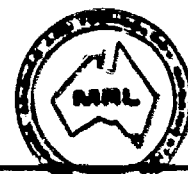


FIGURE 2 Decrease in amine concentration for thermally aged nylon 66 taffeta.



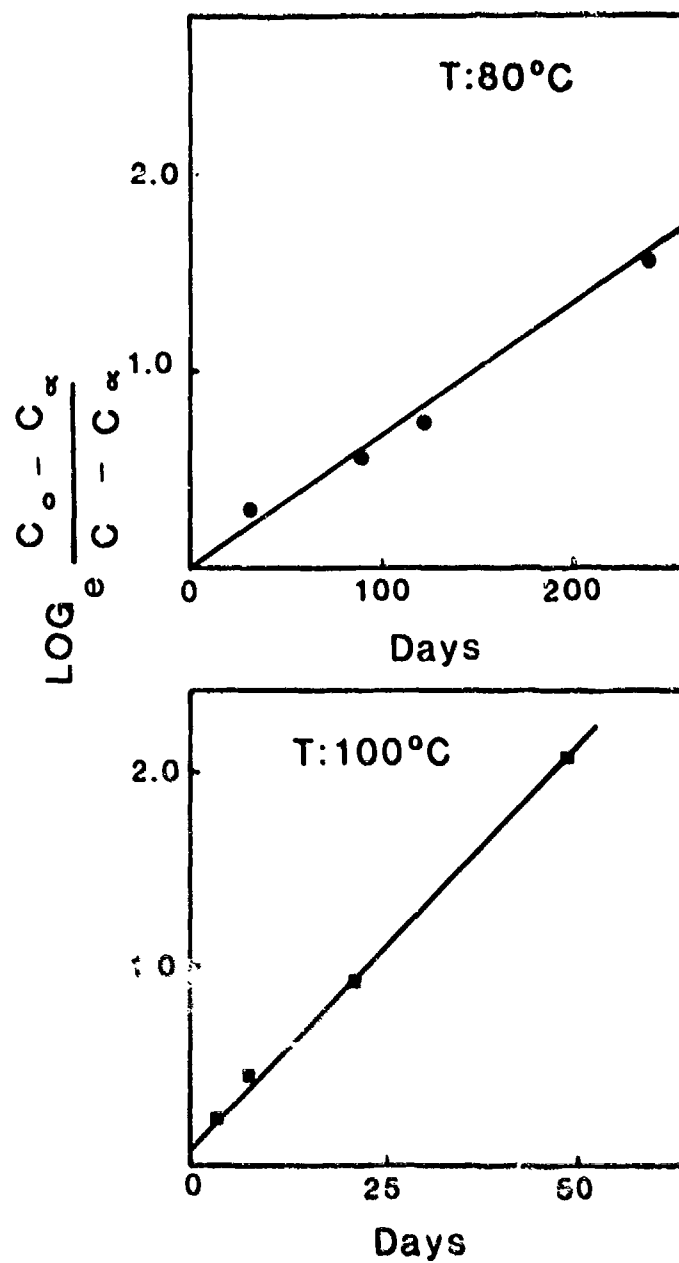


FIGURE 3 First order plot of the disappearance of amine and groups from undyed nylon 66.



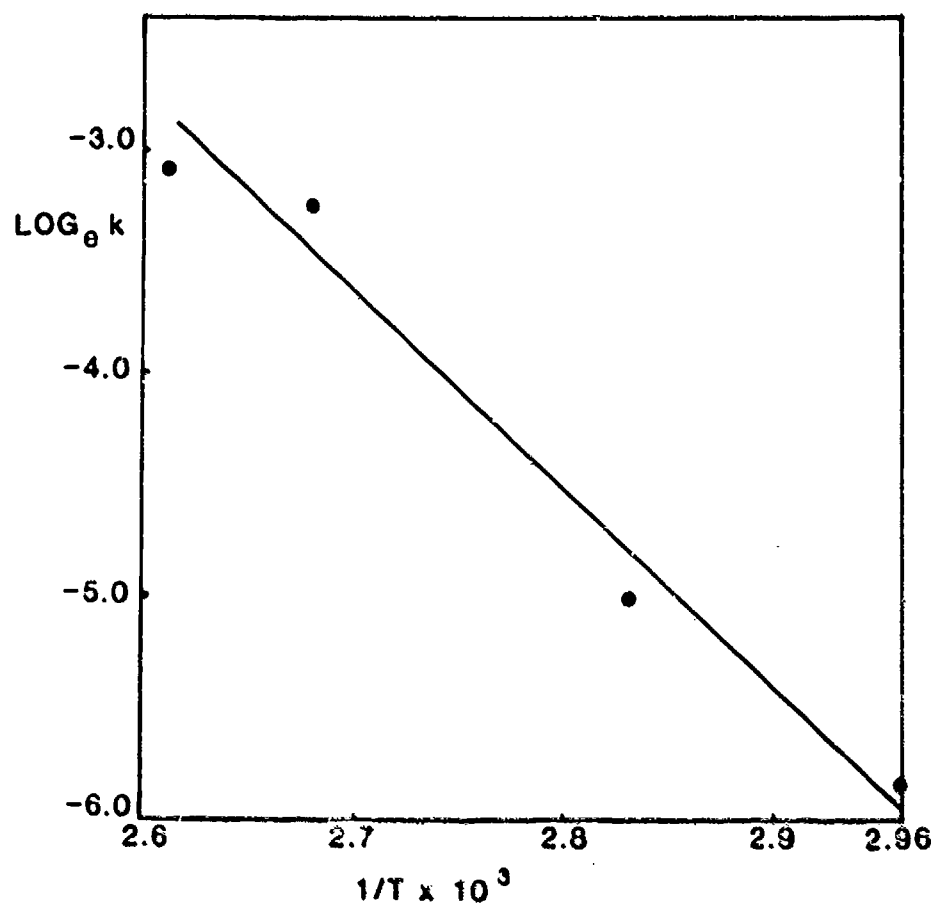


FIGURE 4 Arrhenius Plot of the rate of amine group consumption.



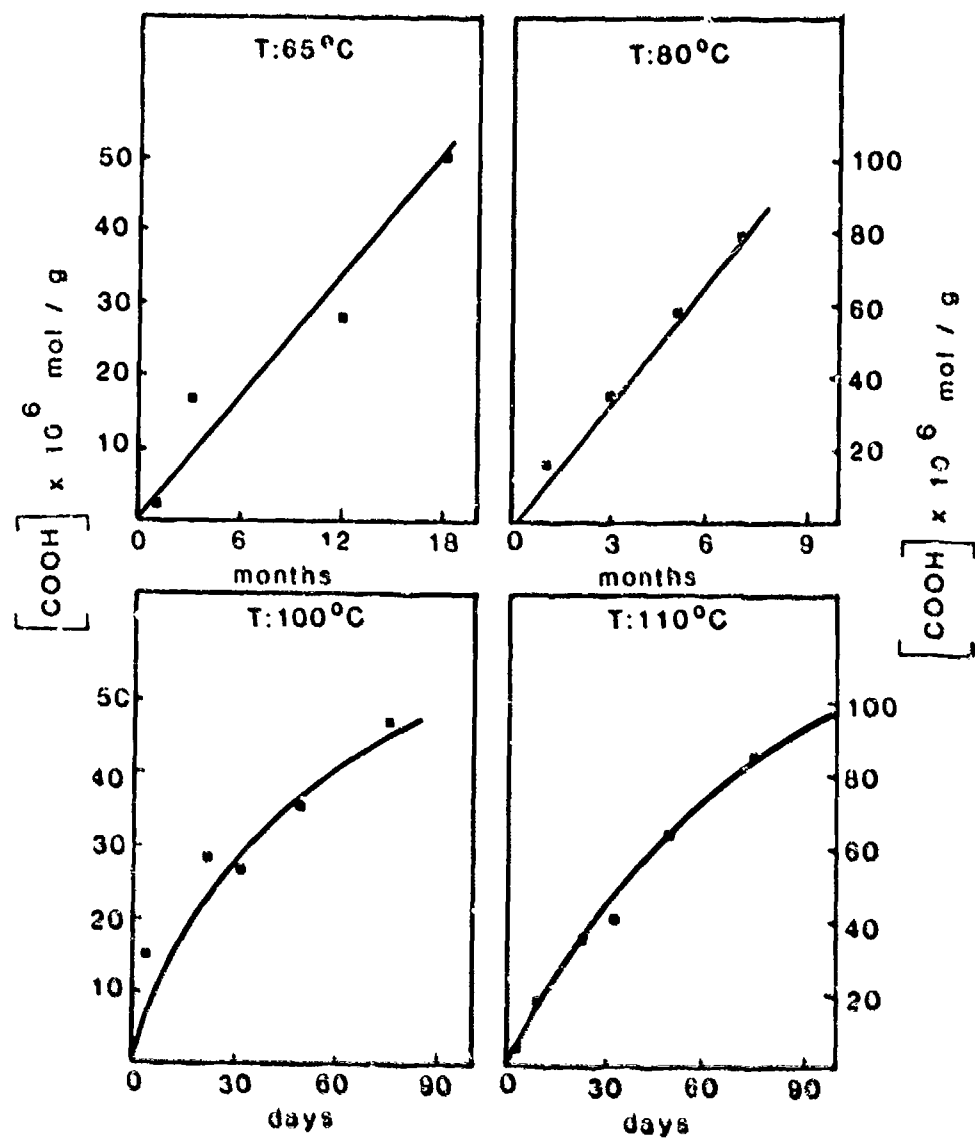


FIGURE 5 Carboxyl Growth [COOH] for undyed nylon 66 at aging temperatures from 65°C to 110°C.



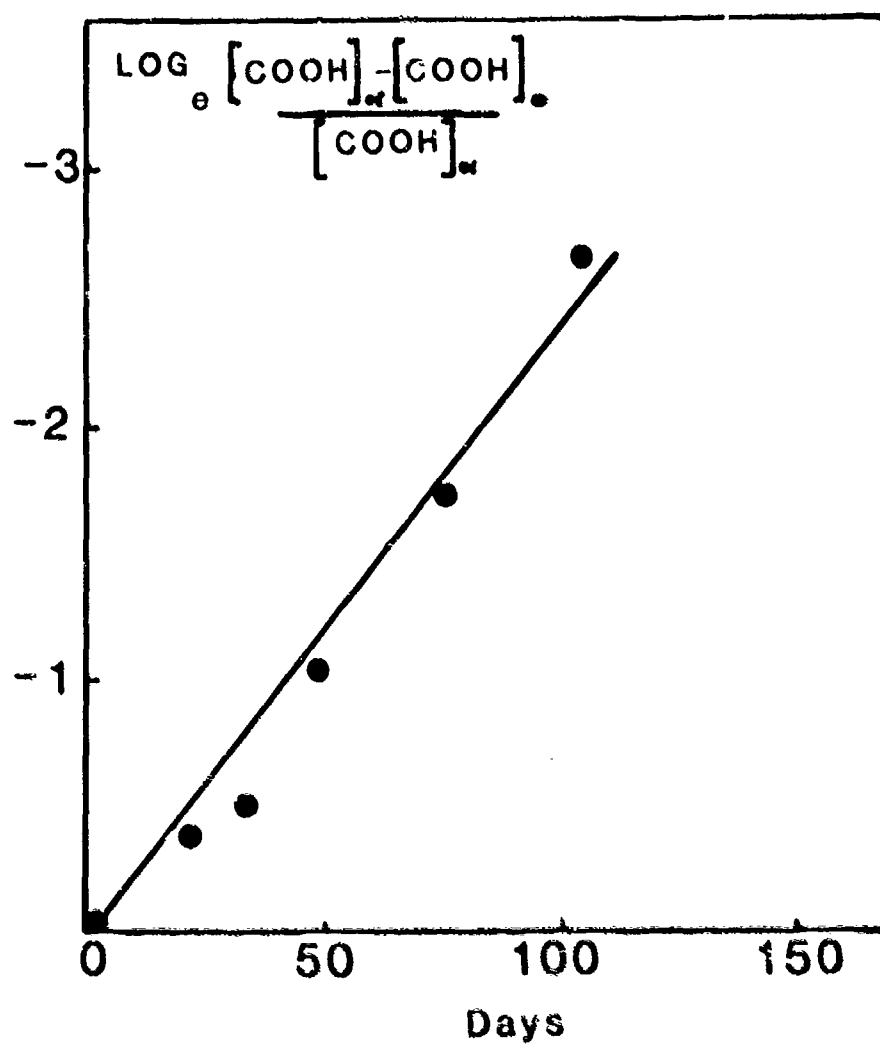


FIGURE 6 First order analysis of the appearance of carboxyl groups in nylon 66 aged at 110°C.



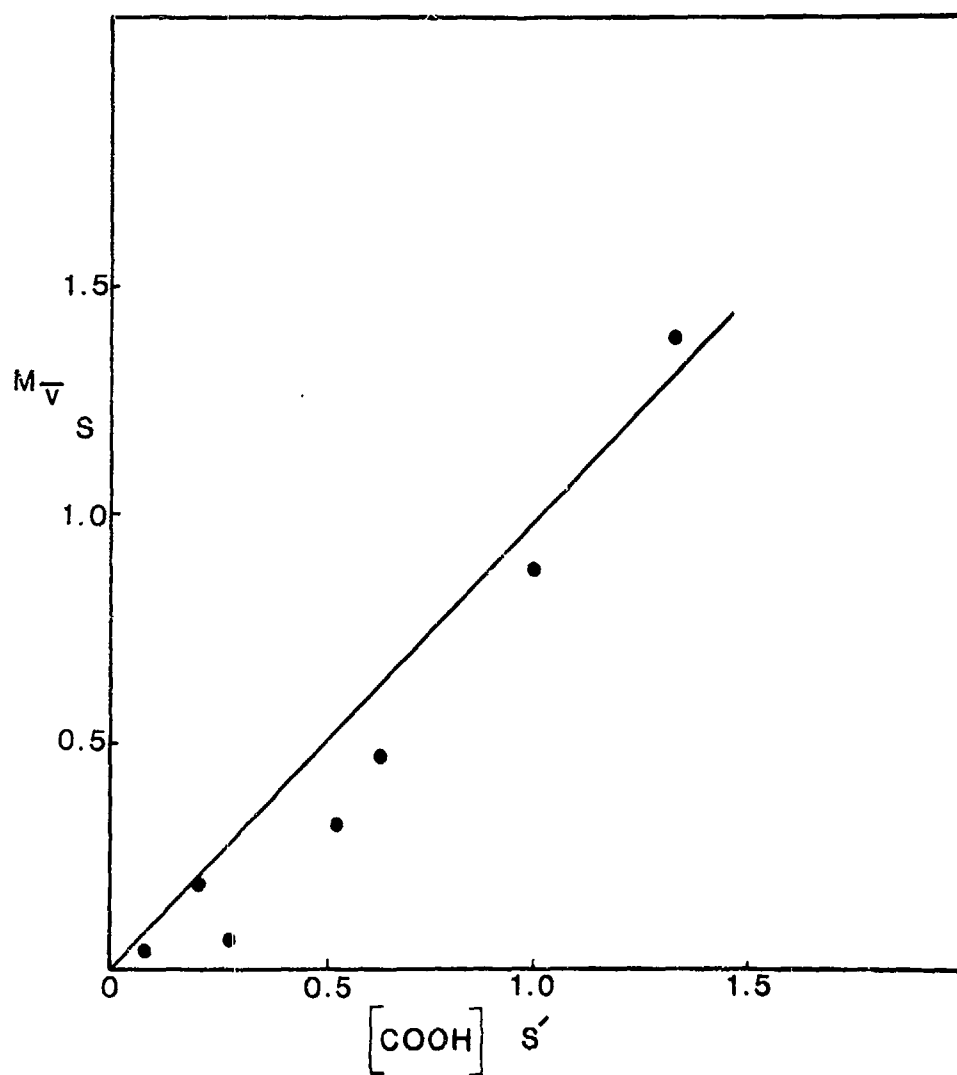


FIGURE 7 Plot of number of polymer chain scissions occurring during thermal aging at 110°C measured by changes in $M_v(s)$ against those determined from $[COOH]$, S' . The line is the 1:1 correlation.



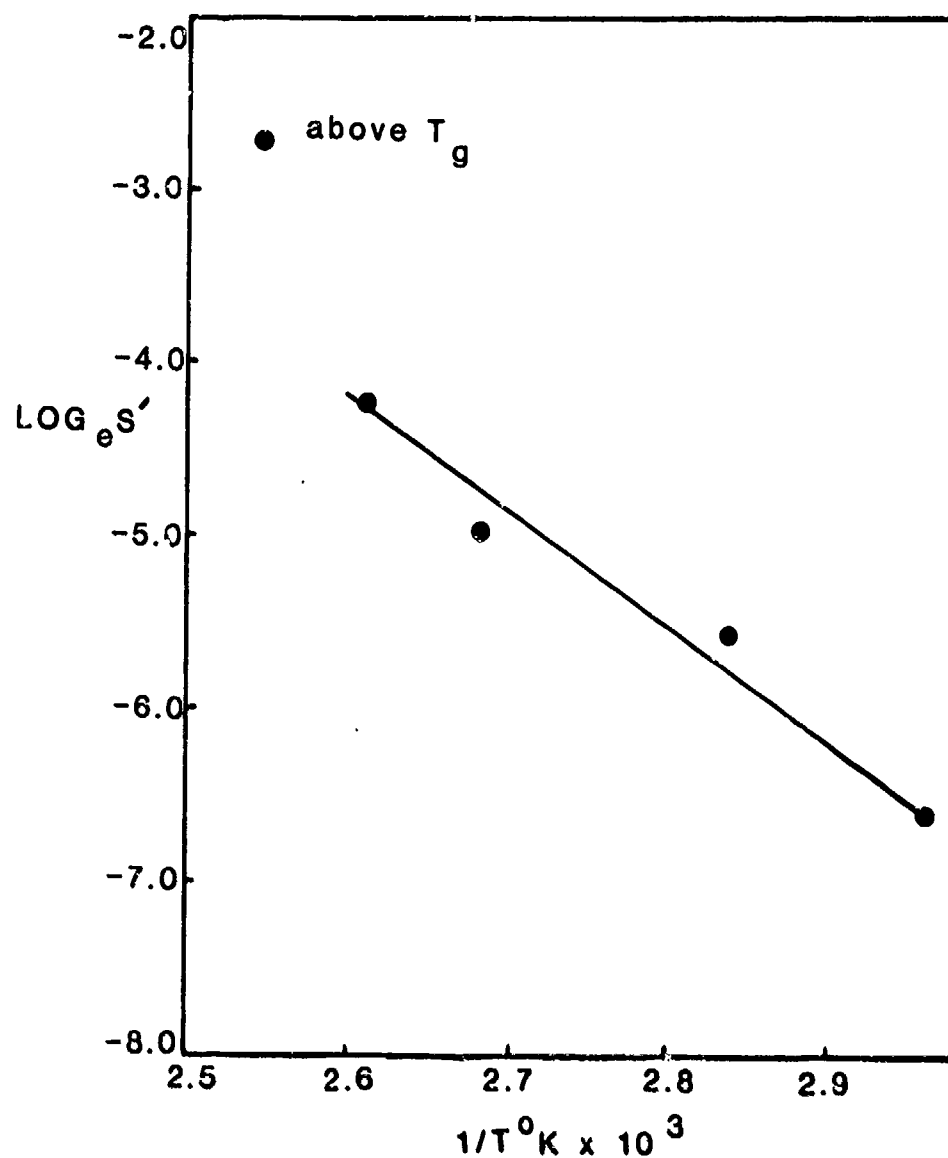


FIGURE 8 Arrhenius Plot of the rate of chain scissions (from [COOH]) for aging temperatures from 65°C to 120°C. Note: The point at 120°C (above T_g) does not fit the Arrhenius relation which is plotted for temperatures from 65°C to 110°C.



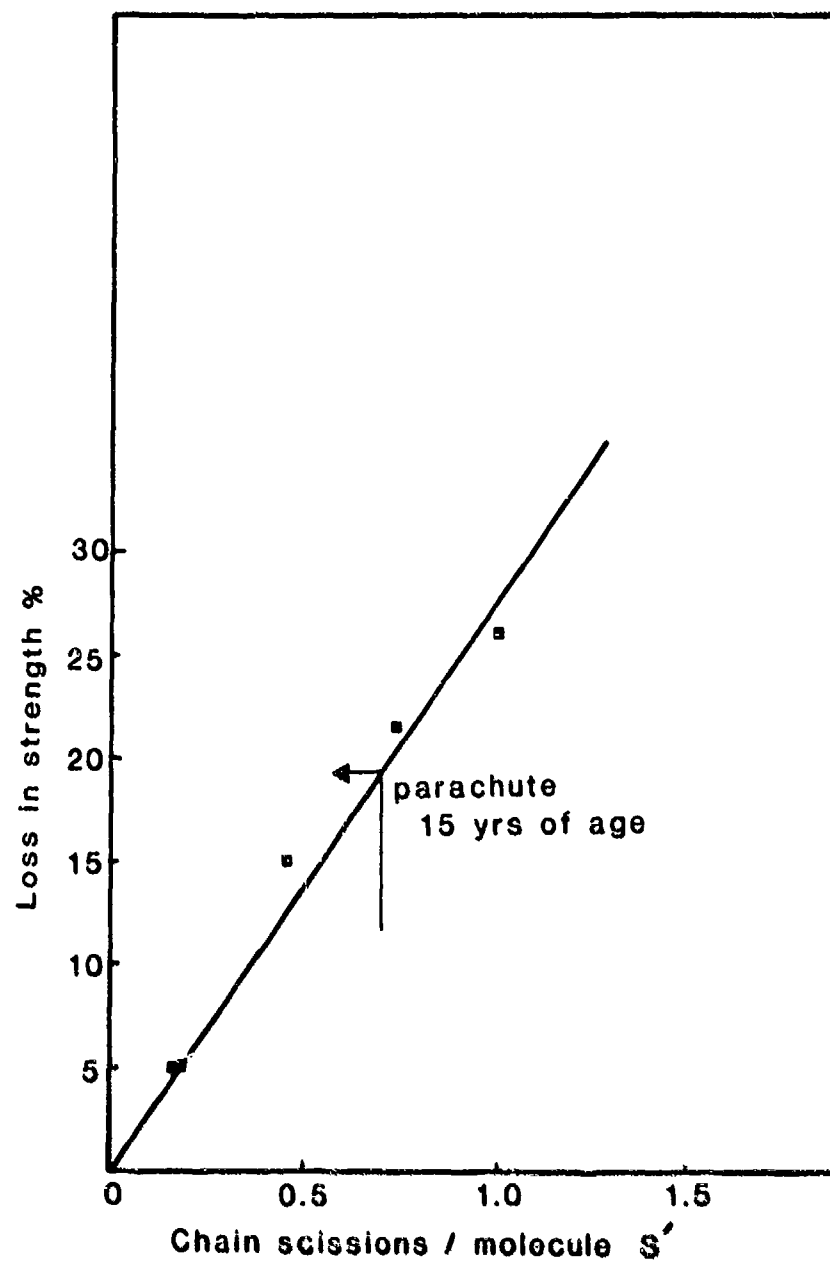


FIGURE 9 Relation between the strength loss from undyed nylon 66 taffeta and polymer chain scissions calculated from carboxyl group concentration after thermal aging at 80°C.



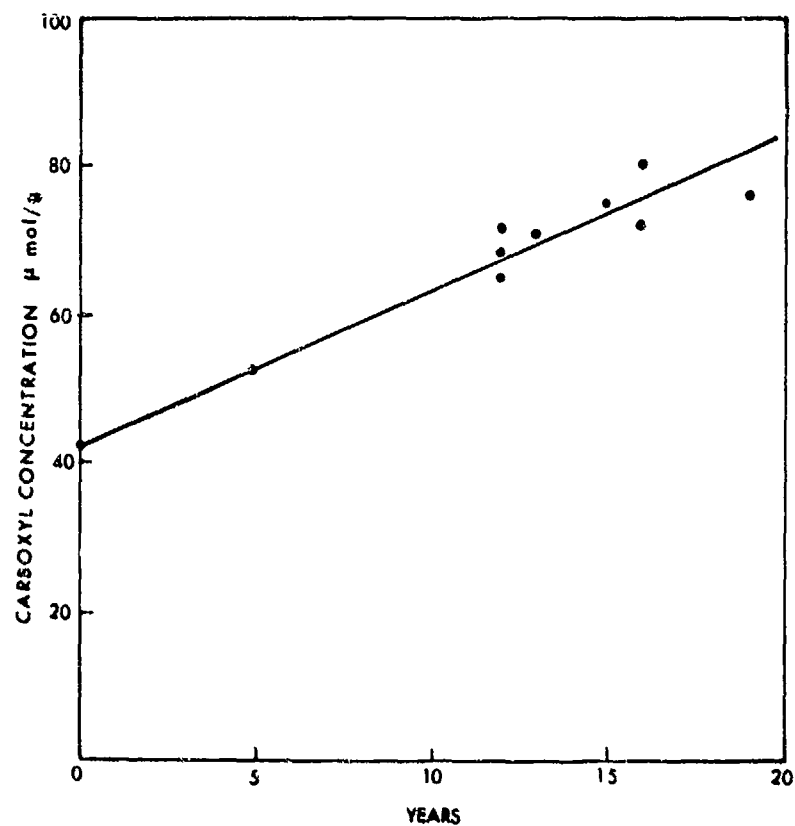
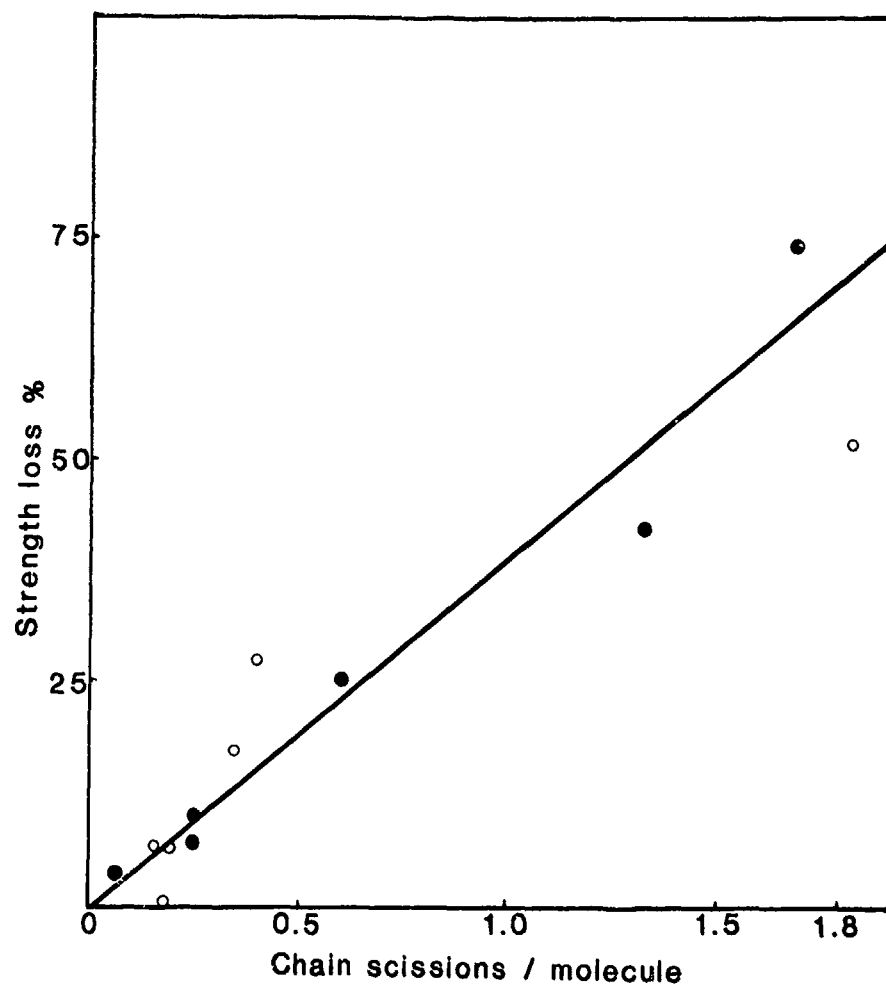


FIGURE 10 Carboxyl group concentration of nylon 66 taffeta canopy material taken from parachutes held in storage for up to 20 years.





- olive drab
- undyed taffeta

FIGURE 11 Relationship between the strength loss (%) and polymer chain scissions calculated from the M_v data for both olive drab and undyed nylon materials on outdoor aging.



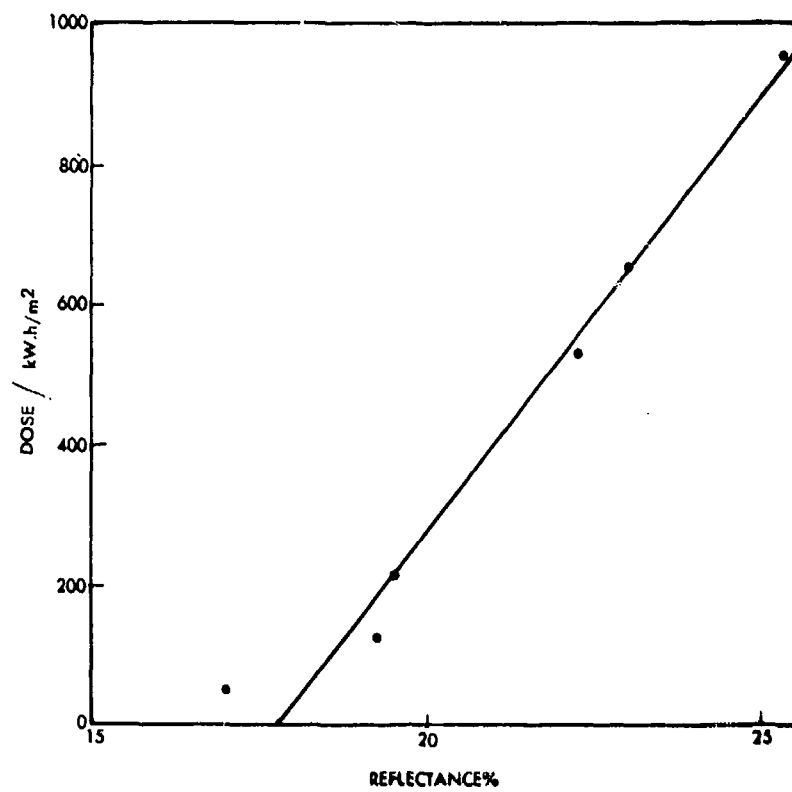


FIGURE 12 Changes in reflectance measurements of photo-oxidised olive drab ripstop material with solar radiation dose.

