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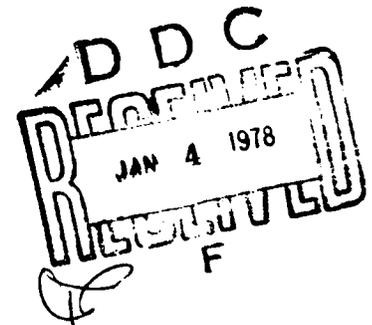
REPORT

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NON-DESTRUCTIVE EVALUATION OF THE DEGRADATION
OF NYLON 6,6 PARACHUTE MATERIALS

G.A. George and N.McM. Browne

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11 G.A./George N.McM./Browne

ABSTRACT

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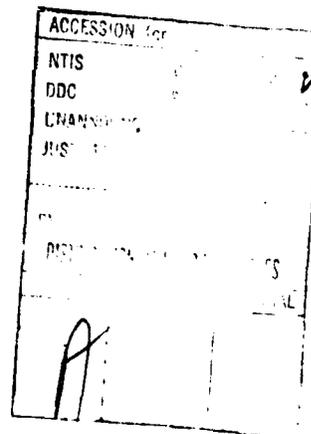
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NON-DESTRUCTIVE EVALUATION OF THE DEGRADATION
OF NYLON 6,6 PARACHUTE MATERIALS

INTRODUCTION

Nylon 6,6 is the principal organic material used in modern troop and cargo parachutes. The excellent mechanical properties of the unprotected fibre are, however, rapidly degraded when the material is subjected to the environmental extremes of sunlight, temperature and humidity (1). Material intended for troop parachutes is specified to be stabilised against thermal and photochemical degradation, but there has been uncertainty in the limits to be placed on the storage and use life of these parachutes.

From a series of engineering investigations, the U.S. Army (2,3) has concluded that there are significant strength losses in nylon components taken from parachutes stored for up to twelve years. These studies involved parachutes that had never been deployed as well as those with a history of up to one hundred descents. In many cases the strength of suspension lines, risers and harnesses had fallen below specification and extension of the age-life was justified only by a consideration of the safety factors inherent in the parachute design. From these investigations the current age limit for the T-10 main parachute has now been designated as fifteen years from manufacture or twelve years in service, and the original limit of one hundred descents has been removed.

The complete engineering evaluation of a parachute requires the destructive testing of a large number of specimens. In the assessment of the extent of degradation of nylon parachute materials stored and used under Australian service conditions it would be desirable to use non-destructive or small-scale sample evaluation to detect the onset of the degradation of critical mechanical properties. Such tests, in conjunction with actual component strength measurements, could then form the basis for age-life limits to be placed on parachutes in service. One possible approach to non-destructive evaluation of nylon 6,6 is to determine, by sensitive spectroscopic methods, the physical and chemical changes occurring in the fibre and the way these affect mechanical properties.

Several fundamental investigations of the *light-induced* degradation of nylon 6,6 have led to an understanding of the relation between the changes in polymer properties, losses in fibre strength and the mechanism

of the oxidation process responsible for deterioration (4,5,6). Thermal degradation is expected to be the dominant factor in the storage life of both main and reserve parachutes. There have been very few studies of the thermal degradation of nylon at temperatures less than 140°C, and conclusions concerning the long-term performance of nylon have been extrapolated from high temperature and light-induced ageing studies (1,6).

In this investigation nylon 6,6 parachute canopy material has been subjected to controlled thermal degradation and the changes in chemical and physical properties related to the loss in breaking strength of the fabric. Particular emphasis is placed on those techniques that are :

- (i) able to detect the changes in fibre properties after short times of degradation,
- (ii) non-destructive or require only a very small amount of material.

The applicability of one of these techniques - phosphorescence spectroscopy - is assessed by a study of canopy material from damaged PB-1 free-fall and life-expired PX-1 troop parachutes.

RESULTS AND DISCUSSION

Actual conditions of service storage and use involve wide temperature variations as well as the interaction of actinic and chemical degradation. No attempt has been made to duplicate actual use cycles, but rather to determine the relationship between fibre strength, morphology, molecular weight and chemical properties after prolonged exposure at an elevated temperature. Limited consideration is given to the interaction of light and heat ageing. Nylon 6,6 semi-dull woven taffeta canopy material was aged for up to 550 days in a forced air oven at $80 \pm 2^\circ\text{C}$ containing silica gel as desiccant. All microscopic, chemical and physical studies, as detailed later in the Experimental Section, were made on the actual samples used for the mechanical properties measurements.

Mechanical Properties

Warp tensile specimens were tested according to DEFAUST 5037 Method A9. As shown in Fig. 1, there was a rapid decrease in breaking force and elongation to break in the first 100 days of exposure, followed by a lower rate of decrease with further exposure. At the final withdrawal (550 days), the samples had lost 46% of the original tensile strength and 52% of the original elongation to break and can be considered highly degraded.

Scanning Electron Microscopy of Failure Surfaces

A study of the fracture morphology of textile fibres by scanning electron microscopy can provide some insight into the causes of failure on environmental exposure (7,8). Figs. 2 and 3 are micrographs of single fibres taken from material aged for 0, 120 and 365 days. Figs. 2a and 2b compare the tensile failure surfaces of single fibres taken from fabric

aged for zero and 120 days, respectively. The unaged sample shows ductile behaviour prior to failure while the aged sample shows little drawing before failure by transverse crack propagation. This is reflected in the 36% decrease in the elongation to break (Fig. 1). The failure appears to be initiated at one of the circumferential microcracks apparent in the aged material. These surface defects are also observed in a sample aged for 120 days that had been cut before mechanical testing (Fig. 3a) and may result from a change in the density of the nylon at the degraded surface. After ageing for 365 days this surface cracking is most severe, as shown in Figs. 3b and 3c for untested and tested samples, respectively. The failure initiation from these surface microcracks is apparent in Fig. 3c where a large crack has opened up a short distance from the actual failure surface in the tensile experiment. In one sample that had been aged for 120 days the failure surface showed evidence of radial crack formation (Fig. 3d). It is uncertain if these initiated from the surface, and the failure mode seems different from that shown in Fig. 2b.

The general conclusion from the micrographs is that thermal ageing produces restructuring of the fibre surface and, consequently, results in microcracks that change the failure mode of the fibre and lower the energy to fracture. These changes are quite distinct from those reported for light-degraded nylon 6,6 (9). In that case the dominant feature is surface pitting from photochemical degradation in the region of the titanium dioxide delustrant, followed by deep void formation throughout the fibre (10). It is thus possible to distinguish the mode of environmental degradation from microscopic examination although the technique cannot presently provide quantitative information as to the extent of degradation.

Molecular Weight

The molecular weight of the undegraded nylon 6,6 has been determined from viscosity measurements (M_v) and end-group analysis (M_n) to be 21400 and 20600, respectively. Thermal ageing at 80°C results in a decrease in molecular weight. In Fig. 4 are plotted the viscosity-average molecular weight and the number of chain scissions per molecule - given by

$(\frac{M_v^0}{M_v} - 1)$ - as a function of the time aged at 80°C. These data suggest

that the observed loss in fibre strength can be directly related to chain scission reactions in the polymer and this is confirmed by the plot shown in Fig. 5. The surface microcracking observed in the electron micrographs probably results from primary bond scission rather than disruption of the hydrogen bonding network without chain scission, as is observed in environmental stress cracking of nylon.

Chemical Changes on Thermal Degradation

The change in the concentration of acid and amine end-groups in the polymer during ageing are shown in Fig. 6. Rapid change in the state of oxidation of the polymer is occurring as amine end-groups are consumed and there is an increase in carboxyl group concentration. This behaviour is similar to that of nylon 6,6 on light-induced ageing (4). The oxidation process occurs as a free radical chain reaction which is discussed in detail in the Appendix. The chain scission reactions that occur in the

termination step of the oxidation lower the molecular weight, disrupt the supermolecular structure of the fibre and decrease the strength. These, and secondary reactions of the oxidation products, result in the formation of end-of-chain carbonyls as aldehydes and acids, in-chain saturated and unsaturated ketones, and nitrogen containing chromophores from reactions of the amine end-groups. The formation of these products is the basis of the spectroscopic methods for the study of nylon degradation. The underlying requirement is that the extent of oxidation of the nylon material as determined by a specific technique should be directly related to the loss in mechanical properties.

Reflectance Spectra

The presence of polymer oxidation products in degraded materials has frequently been detected by attenuated total reflectance infra-red spectroscopy (11) (ATR-IR) using the appearance of the characteristic aliphatic carbonyl absorption around 1700 to 1730 cm^{-1} . In this investigation no evidence could be found for the appearance of this or other oxidation products, the ATR-IR spectrum from material aged 550 days being superimposable on that from unaged nylon over the range 4000 cm^{-1} to 400 cm^{-1} . Significant changes were observed in the UV-visible diffuse reflectance spectrum, as shown in Fig. 7. The enhanced sensitivity in this spectral region over that in the infra-red may reflect the higher extinction coefficients for the electronic transitions of the conjugated oxidation products (due to mixed $n\pi^*$ and $\pi\pi^*$ character) believed responsible for the absorption properties of degraded nylon (see Appendix). In addition, the absence of underlying amide absorption bands improves the sensitivity of the electronic spectrum over the infra-red. The transmission UV spectrum of the nylon taffeta in methanol:HCl solution (1:1) shows only weak absorption in the region 400 to 320 nm (Fig. 8) and the appearance of a strong band with a maximum at 280 nm. This spectrum is identical to that observed (12) from light-aged nylon 6,6 and, as discussed in the Appendix, it is assumed that similar chromophores are responsible for the absorption and reflectance spectra reported here.

The relation between the extent of polymer oxidation as measured by reflectance spectra and the loss in fabric strength is shown in Fig. 9. The technique appears insensitive to changes in tensile strength at short times of ageing which would limit its applicability as a method of non-destructive evaluation. Direct measurement of the solution absorption spectrum provides a more sensitive method of detecting oxidation products (Fig. 8) but requires destructive testing of the fabric.

Phosphorescence Spectra

Emission spectroscopy has been used recently to detect the low concentrations of oxidation products present in polymers during environmental degradation (13,14). The increased sensitivity over absorption techniques and the characteristic phosphorescence spectra associated with carbonyl compounds permits the early stages of the degradation of nylon 6,6 to be studied. In Fig. 10 are shown a series of phosphorescence spectra from nylon 6,6 taffeta aged for the time indicated. The following observations are made :

(i) On excitation with 290 nm radiation, an emission spectrum with a maximum at 403 nm and lifetime (τ_e) of 2.2 s is observed from unaged nylon. The origin of this emission spectrum is uncertain, but is believed to be due to chromophores formed in the melt polymerization and/or spinning process (15). On thermal degradation this maximum decreases in intensity and shifts to longer wavelength as an underlying band at 460 nm increases in intensity.

(ii) On excitation with 320 nm radiation, only the emission centred at 460 nm is observed. It is seen that the original unaged nylon shows low emission intensity in this region and the intensity increases on thermal degradation. The lifetime of this emission is 0.7 s. This spectrum has been assigned to α, β -unsaturated carbonyl oxidation products (15) formed in termination reactions of the oxidation sequence described in the Appendix.

The determination of the concentration of oxidation products from the emission spectrum of a degraded polymer film can be as reliable as that from absorption spectra under controlled conditions. The errors in measurement of a fabric are somewhat greater due to light scattering, but reliable and reproducible intensity data have been obtained using the procedures outlined in the experimental section.

The concentration, C , of absorbing chromophores can be related to the integrated phosphorescence emission intensity, I_p , by (14)

$$C = \frac{I_p}{2.303 k \phi_p I_o \epsilon d}$$

where I_o is the exciting light intensity,

ϕ_p is the phosphorescence quantum yield,

ϵ is the molar extinction coefficient of the absorbing species at the excitation wavelength,

d is the sample thickness,

and k is a geometrical and instrumental constant.

Neglecting phosphorescence quenching effects, these constants can be accumulated to

$$C = K I_p / I_o$$

Figs. 8 and 10 show that the unaged nylon taffeta contains a low concentration of the thermal oxidation product with an emission maximum at 460 nm. If this concentration is C^0 and the concentration at any time, t , during the thermal degradation is C^t , the increase in carbonyl chromophore concentration is :

$$\begin{aligned}
C^t - C^o &= K/I_o \left(I_p^t - I_p^o \right) \\
&= C^o \left(\frac{I_p^t}{I_p^o} - 1 \right)
\end{aligned}$$

where I_p^t and I_p^o are the emission intensities from the degraded and unaged samples, respectively. Thus a plot of $\left(\frac{I_p^t}{I_p^o} - 1 \right)$ against loss in strength should give a standard curve from which the extent of degradation of an unknown sample can be measured directly from its phosphorescence spectrum.

Fig. 11 is such a plot based on emission intensity at 460 nm and excitation at 290 nm. In this case the measured intensity is the sum of the emission from the α, β -unsaturated carbonyl oxidation product having its maximum at this wavelength and the long wavelength tail of the intrinsic nylon emission. This latter component is subtracted from the spectrum on the assumption that the spectral distribution of the intrinsic emission is unaltered on ageing. On excitation at 320 nm this emission is not excited, so the actual carbonyl emission intensity integrated over all wavelengths can be calculated. The resulting standard curve is shown in Fig. 12. The scatter in the data points from this method is greater than that in Fig. 11 because of the lower emission intensity on 320 nm excitation.

Non-destructive Evaluation of Canopy Materials by Phosphorescence

The phosphorescence technique has been assessed by two separate studies of nylon 6,6 canopy material returned from service. These were panels from two life-expired PX-1 personnel parachutes aged thirteen years from the date of manufacture and panels from two PB-1 free fall parachutes, one of which had experienced tearing during deployment. From the measured phosphorescence spectra an estimate was made of the loss in strength of these materials compared with the unaged nylon taffeta by reference to the curve of Fig. 12. These were then compared with actual mechanical strength measurements.

(i) PX-1 Personnel Parachutes

Phosphorescence spectra were measured with 320 nm excitation of sections of panels from PX-1 canopies manufactured in December 1963 and May 1964. The integrated emission intensities were identical within

experimental error and the average emission index $\left(\frac{I_p^t}{I_p^o} - 1 \right)$ was 0.59.

As indicated in Fig. 12 this corresponds to a strength loss of 19.5%. The average breaking load for these fabrics was 407 N, which is a strength loss of 16.25% based on the breaking load of unaged taffeta of 486 N (Fig. 1). The agreement with the emission technique is good, considering the experimental uncertainty of the data of Fig. 12. These strength loss measurements also suggest that extrapolation from the accelerated ageing data collected at 80°C to the actual storage conditions is valid. From Fig. 1, the strength loss corresponds to an ageing time at 80°C of 90 to 100 days. Assuming that the degradation rate can be fitted to the Arrhenius rate equation smoothly over the temperature range from 80°C to 20°C, this corresponds to an average degradation temperature of about 25°C for thirteen years.

(ii) *PB-1 Free Fall Parachutes*

Panels taken from canopies of PB-1 parachutes coded F119 and F134, with a history of 22 and 24 jumps respectively, were studied. A large area of F134 had shown severe tearing during deployment. Breaking load measurements from both sound and damaged areas of F134 and F119 showed the same strength loss of 14% compared to the unaged nylon taffeta. Phosphorescence spectra of these samples gave an emission index of 0.7 and 0.54, respectively for F119 and the sound area of F134. As shown in Fig. 12 these are similar to the values obtained for the PX-1 parachute materials. The damaged panel of F134, however, gave an index of 1.2 showing that it was quite highly oxidised, and would have a predicted strength loss of 35%. Whether this can explain the failure of the panel when subjected to the opening forces on deployment is unknown. It is surprising that the mechanical measurements showed no greater strength loss than for the undamaged canopies, since the sample for emission analysis was taken from the actual tensile test strip.

It was noted that some areas of the F134 canopy showed localised burn damage, and the possibility that the oxidation observed could result from localised heating on suspension line run-over was considered. Swallow (16) has studied the simulation of the searing of nylon canopy material by suspension line and the effect on mechanical properties. This method was followed here by searing a section of unaged nylon taffeta which was brought in contact for one second with nylon suspension line running at 16 m/s. Microscopic examination revealed localised melting of the fibres at the contact point. Examination of a large area around the contact point by phosphorescence spectroscopy showed no change in the emission index. It is concluded that the rapid heating to a local temperature greater than the melting point of 260°C, and subsequent cool down in the space of a few seconds, allows little oxidation to occur, and the increased oxidation observed in the torn area of F134 does not result from suspension line damage.

Limitations to Spectroscopic Evaluation

The spectroscopic techniques of diffuse reflectance and phosphorescence, while essentially laboratory methods, can potentially be modified for routine non-destructive evaluation. Both methods sample small areas - reflectance approximately 2 cm² and phosphorescence from 0.01 to 2 cm² - so a sampling technique is required for the evaluation of the many square

metres of parachute material. It is possible that a sampling approach may not detect degraded areas, or the sample tested may be not truly representative of the unit as a whole. This limitation has been considered most important by the U.S. Army (3) who, moreover, consider the prospect for a reliable system for economical, on-site, non-destructive evaluation to be rather remote. At the present state of instrumentation and understanding of material degradation, these spectroscopic techniques are best used for observing systematic material property changes on storage or controlled use, rather than for in-service monitoring.

CONCLUSIONS

The thermal degradation of nylon 6,6 canopy fabric for periods up to 550 days at 80°C results in strength losses of up to 46%. Scanning electron micrographs of degraded fibres show that microcrack formation lowers the fibre fracture energy, so degrading the mechanical properties. This strength loss is linked to the rapid decrease in polymer molecular weight from chain scission reactions on oxidation at the elevated temperature. Reflectance, absorption and emission spectra have been used to evaluate the extent of oxidation of the fabric and to relate it to the loss in strength. The phosphorescence emission index has been used to non-destructively determine the extent of degradation of life-expired PX-1 and damaged PB-1 canopy materials.

EXPERIMENTAL

Materials

The nylon 6,6 parachute canopy material was a taffeta of 47.5 g/m² having 44 ends/cm and 44 picks/cm plain woven from 45 denier, 15 filament yarn with 0.28% titanium dioxide (rutile) as delustrant.

Molecular Weight Measurements

Viscosity-average molecular weight, \bar{M}_v , was determined by dilution viscometry in m-cresol at 25°C. The values of $K = 0.24 \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.61$ were used in the Mark-Houwink equation (17). The titanium dioxide was removed by centrifugation.

End-group analysis was performed by the method of Waltz and Taylor (18). For acid end-groups the fabric was dissolved in benzyl alcohol at 180°C and titrated to a phenolphthalein end-point with standardised 0.1 N potassium hydroxide in methanol/benzyl alcohol. A blank run was used to correct for the oxidation of benzyl alcohol in this temperature. Amine end-groups were determined by conductometric titration of a phenol/alcohol/water solution of nylon 6,6 with standard hydrochloric acid. If a and b are the acid and amine end-group concentrations in equivalents per gram of then $M_n = \frac{2}{a+b}$. Delustrant was not removed for end-group analysis.

Reflectance and Absorption Spectra

Diffuse reflectance spectra were obtained using an R-10A integrating sphere accessory in an Hitachi EPS-3T recording spectrophotometer. Absorption spectra of 1g/dl solutions of nylon taffeta in methanol: HCl (1:1) were obtained with a Varian 635 spectrophotometer. Suspended titanium dioxide was removed by centrifugation.

Phosphorescence Spectra

Emission spectra were obtained at 77°K using apparatus of the type previously described (19). Both front-face (45° angle between incident excitation and emission beams) and back face (180° angle) spectra were recorded using normal incidence to minimise changes in scattering losses from sample to sample. Lamp fluctuations were corrected by continuous monitoring of part of the excitation beam with a Rhodamine B/phototube intensity monitor. The reported spectra were not corrected for the spectral sensitivity of the analysing monochromator and photomultiplier. Low UV excitation intensity was used to minimise the possibility of photochemical reaction during spectrum measurement.

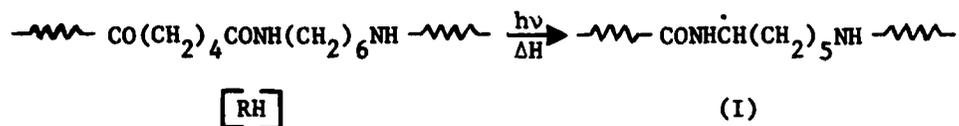
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APPENDIX

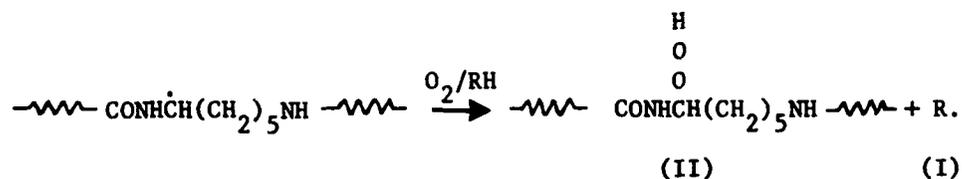
The Mechanism of Thermal Oxidation of Nylon 6,6

Fundamental studies of the auto-oxidation of poly(hexamethylene adipamide) - nylon 6,6 - have been carried out principally by UV initiation (1). Thermal initiation, since it occurs through decomposition of trace hydroperoxide or similar impurity groups, rather than direct amide group or impurity centre photolysis, should be considerably slower. In both cases the primary step in the free radical oxidation sequence is the formation of the alkyl radical (I) by attack on the methylene group α to the amide.



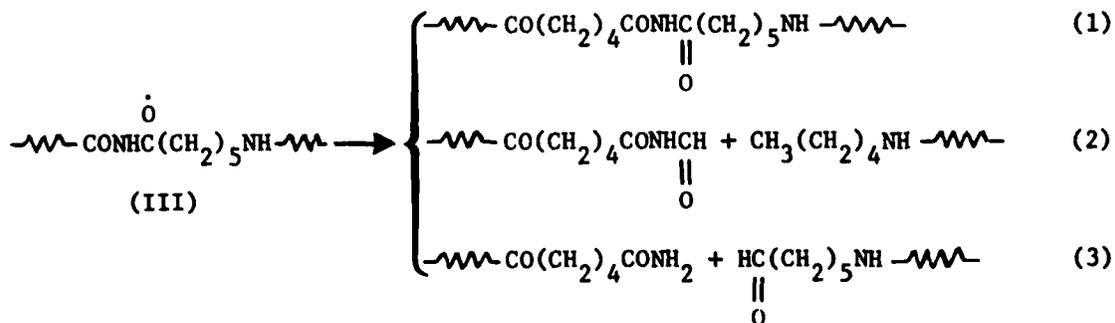
INITIATION

The propagation reactions of radical (I) with oxygen produces a peroxy radical which abstracts a hydrogen atom from an α -methylene group of another chain to produce another radical (I) and a hydroperoxide (II).



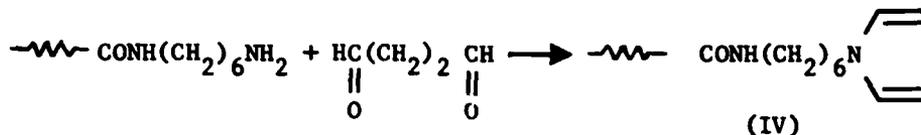
PROPAGATION

Thermal or photochemical decomposition of the hydroperoxide to the alkoxy radical (III) leads to the following possible chain termination reactions.



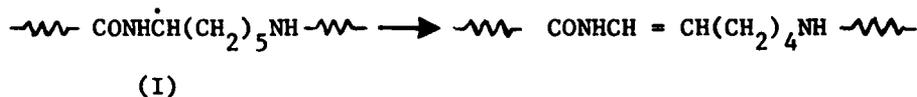
TERMINATION

Reactions (2) and (3) produce one carbonyl end-group per chain scission while reaction (1) produces an in-chain carbonyl. Further reaction of this species has been proposed (12) as a route to succinic dialdehyde which will react with an amine end-group of the polyamide to produce a pyrrole (IV).

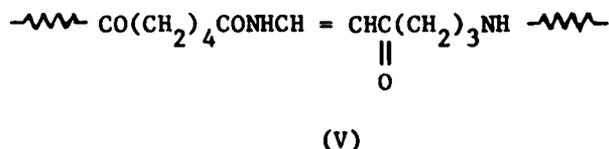


The species (IV) had been proposed (12) as the source of the yellow colouration in degraded nylon 6,6 (see reflectance spectrum, Fig. 7). However, spectroscopic studies (20) have shown that, when pure, (IV) does not absorb at 280 nm as had been believed, and it is possible that the observed absorption spectrum shown in Fig. 8 corresponds to secondary oxidation products such as maleimides (21), which absorb strongly at 280 nm with a spectrum identical to that observed here.

Other species that form on thermal oxidation, and are not observed on photo-oxidation, are believed to be α,β - unsaturated carbonyls (15). The precise mechanism for formation has not been reported, but it could occur by a rearrangement reaction of radical (I) prior to formation of a peroxy radical.



Subsequent oxidation of the methylene adjacent to the unsaturation produces the unsaturated carbonyl (V) by the termination reaction (1).



Such species are photolytically unstable (22) and, in the polymer, may rearrange to a β,γ - unsaturated ketone or undergo crosslinking reactions on UV irradiation (23). Since the phosphorescence analysis technique reported here determines the extent of polymer oxidation by measuring emission from the chromophore (V), it is important to recognise the effect that a combination of light and thermal degradation can have on the measured emission intensity. On long term storage the effect of UV radiation is negligible, and this is reflected in the results reported here for the life-expired PX-1 parachute canopies.

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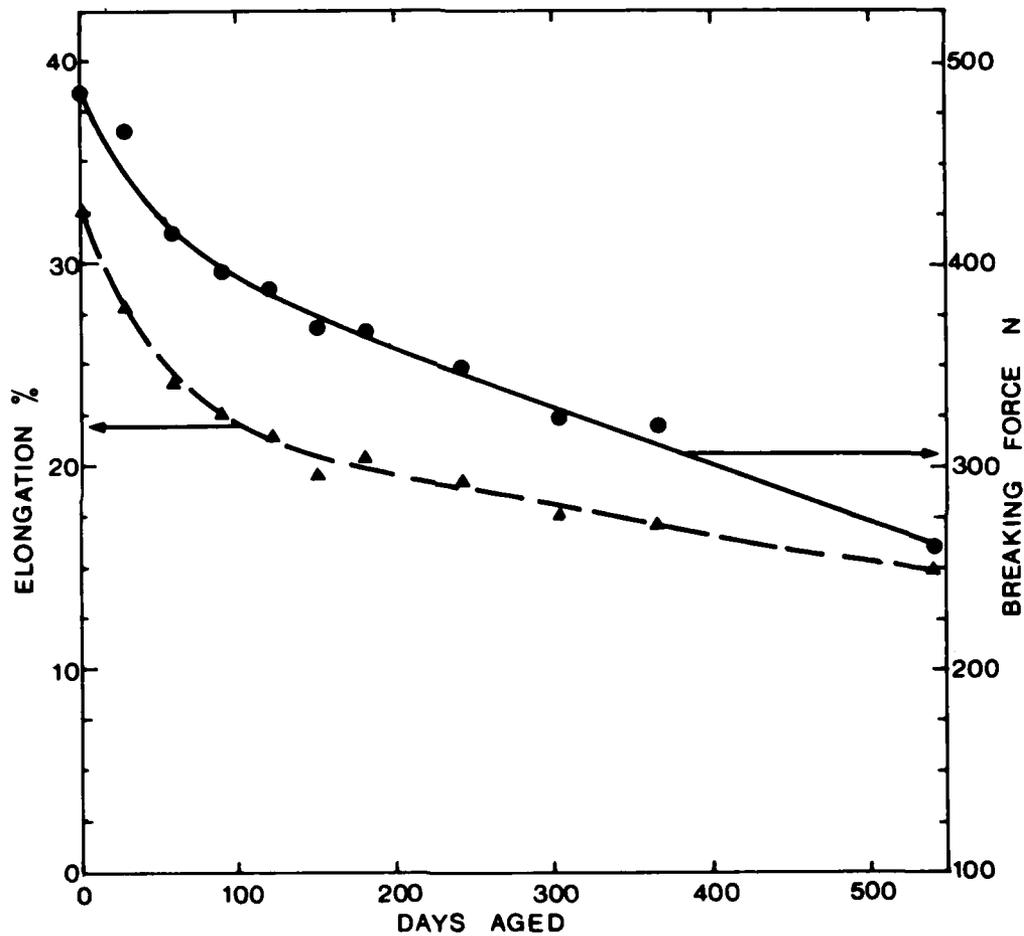
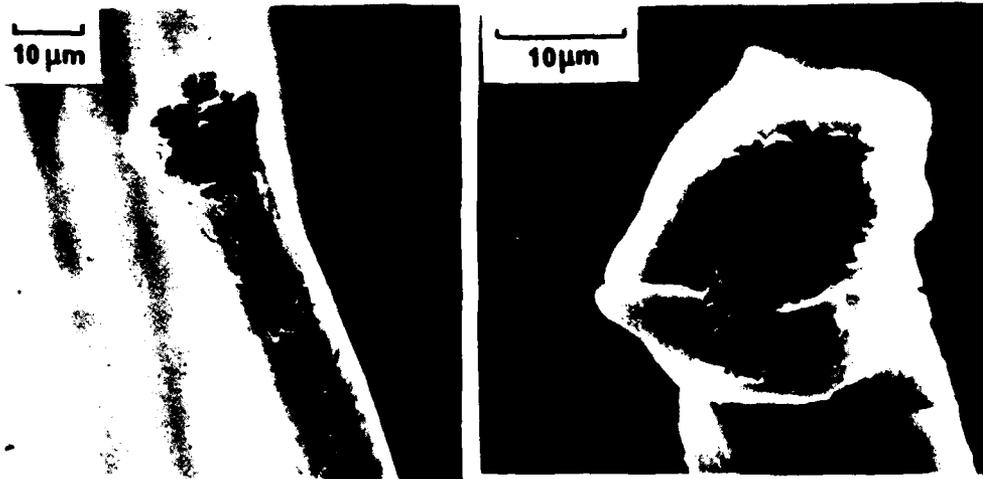


FIG. 1 - The mechanical properties in the warp direction of nylon 6,6 taffeta canopy fabric (5 cm strip) as a function of time of ageing at 80°C.



(a)



(b)

FIG. 2 - Scanning electron micrographs of single fibres from nylon 6,6 taffeta aged at 80°C.

(a) Unaged. Tensile failure.

(b) Aged 120 days. Tensile failure.

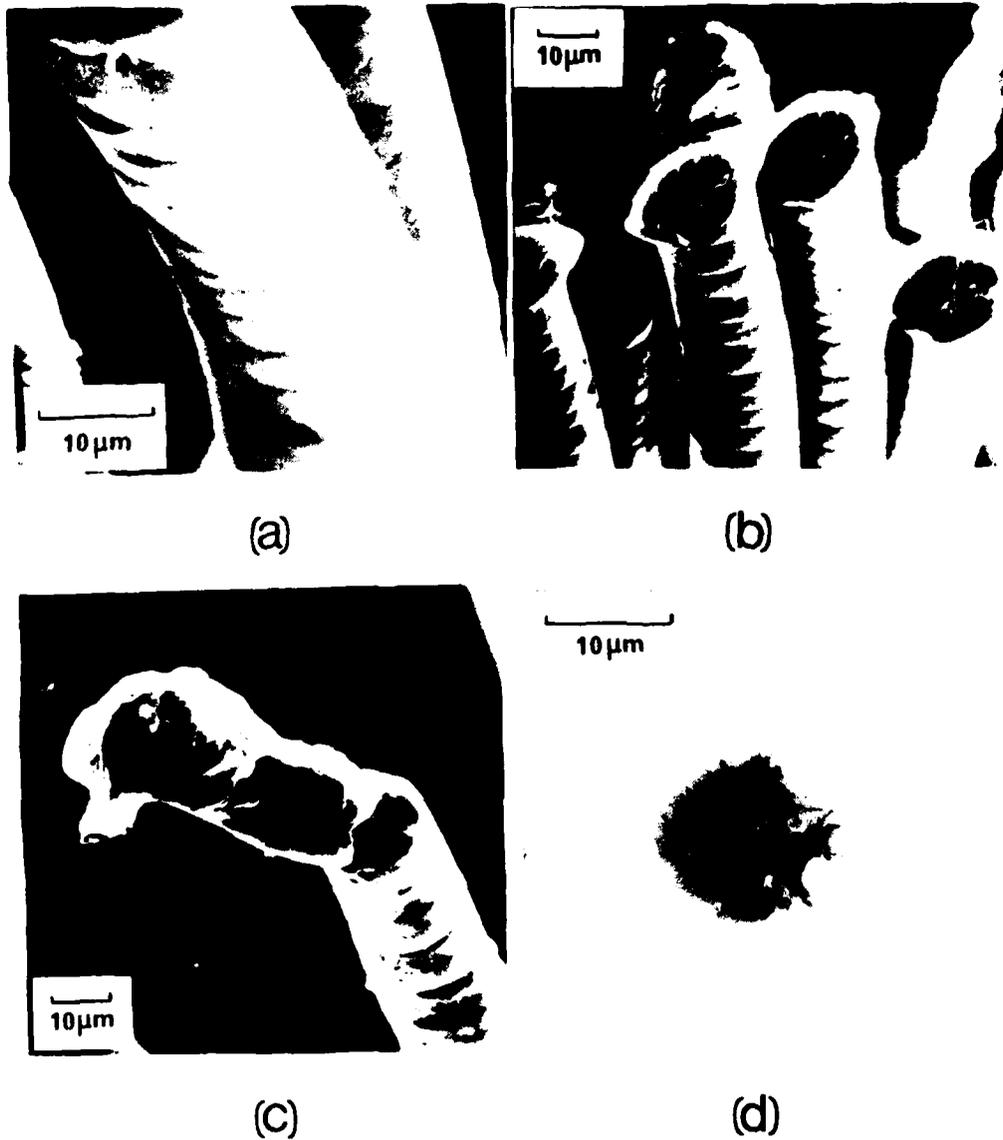


FIG. 3 - Scanning electron micrographs of single fibres from nylon 6,6 taffeta aged at 80°C.

- (a) Aged 120 days. Fibres cut.
- (b) Aged 365 days. Fibres cut.
- (c) Aged 365 days. Tensile failure.
- (d) Aged 120 days. Tensile failure.

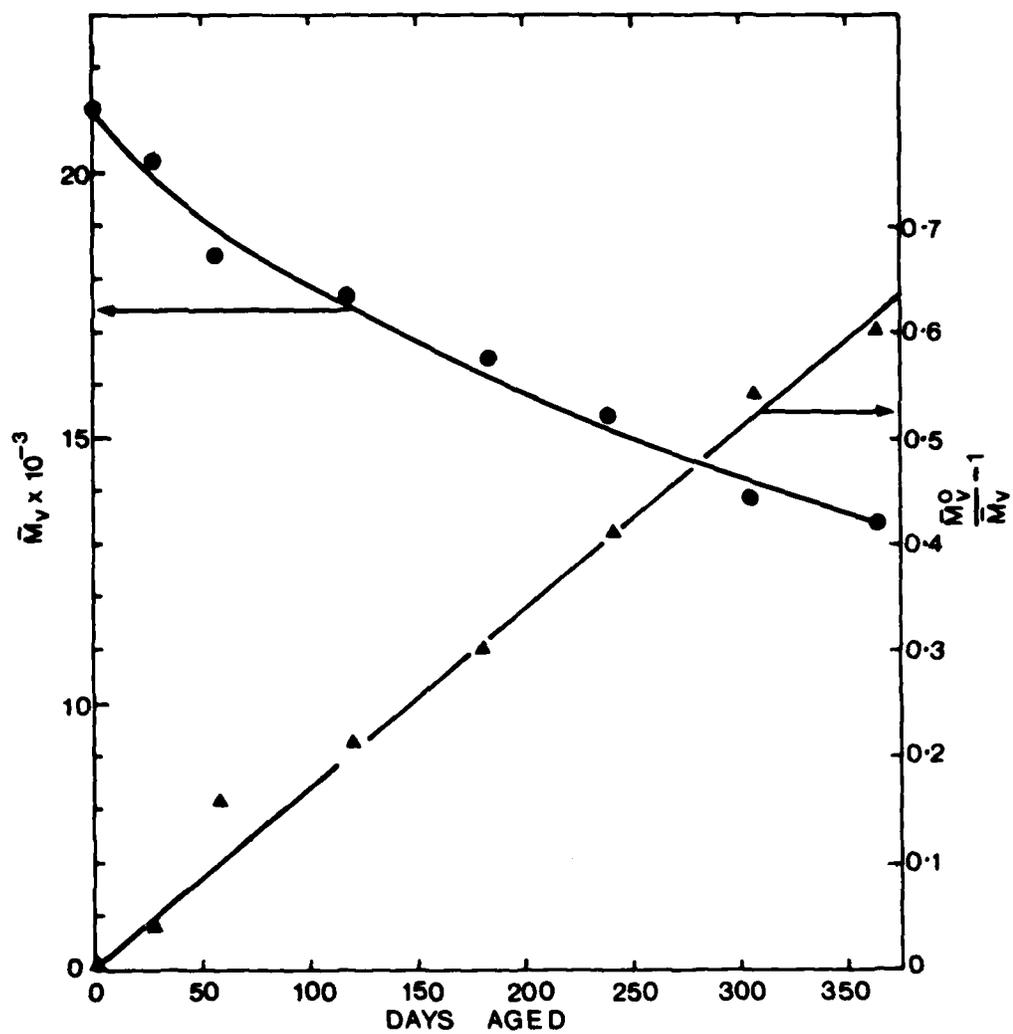


FIG. 4 - Viscosity-average molecular weight (\bar{M}_v) and number of chain scissions per molecule ($\frac{\bar{M}_v^0}{\bar{M}_v} - 1$) of nylon 6,6 taffeta as a function of time of ageing at 80°C.

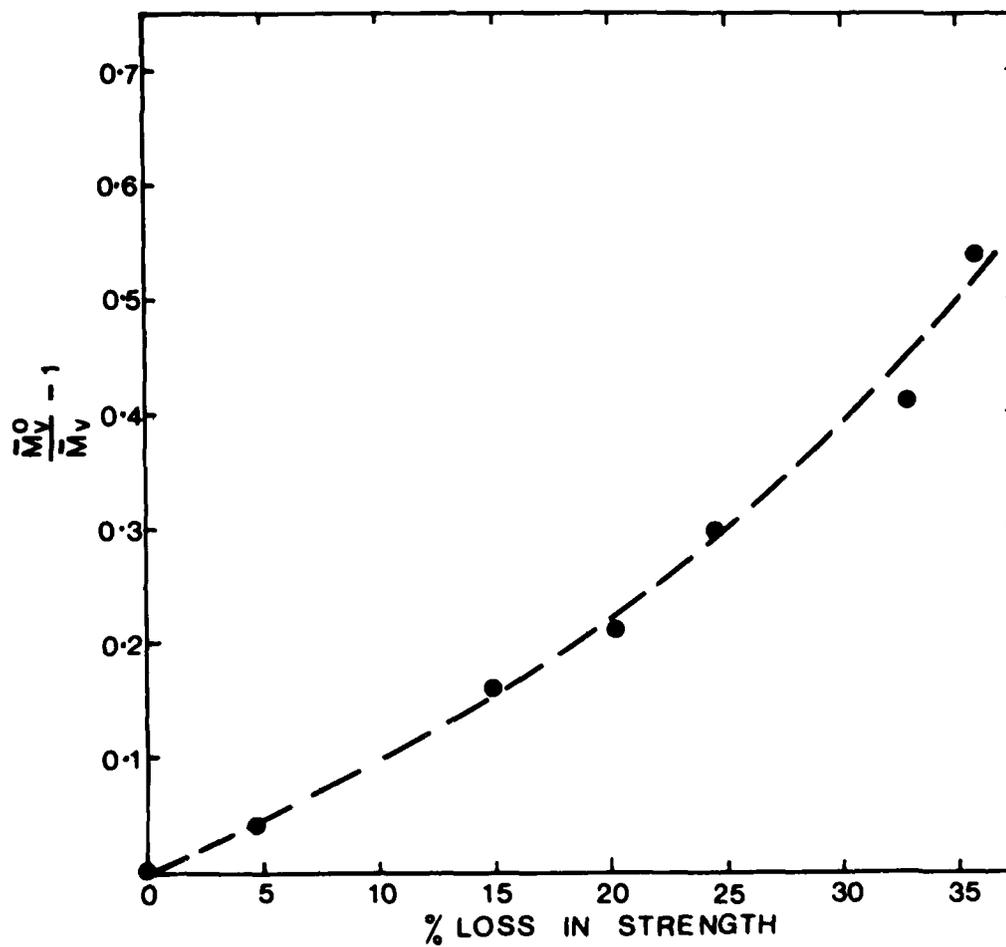


FIG. 5 - The relation between loss of strength on ageing and the number of chain scissions per molecule $(\frac{\bar{M}_v^0}{\bar{M}_v} - 1)$ of nylon 6,6 taffeta.

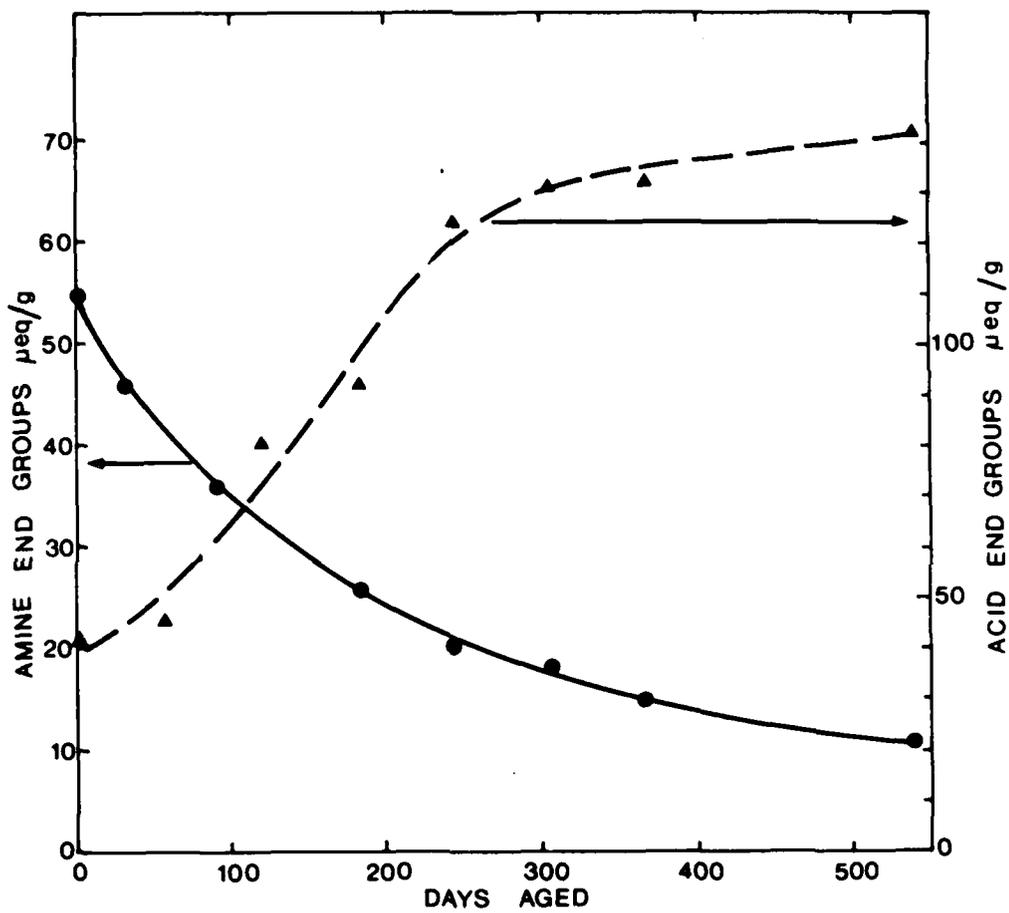


FIG. 6 - The concentration of acid and amine end groups (micro equivalents/g) in nylon 6,6 taffeta as a function of time of ageing at 80°C.

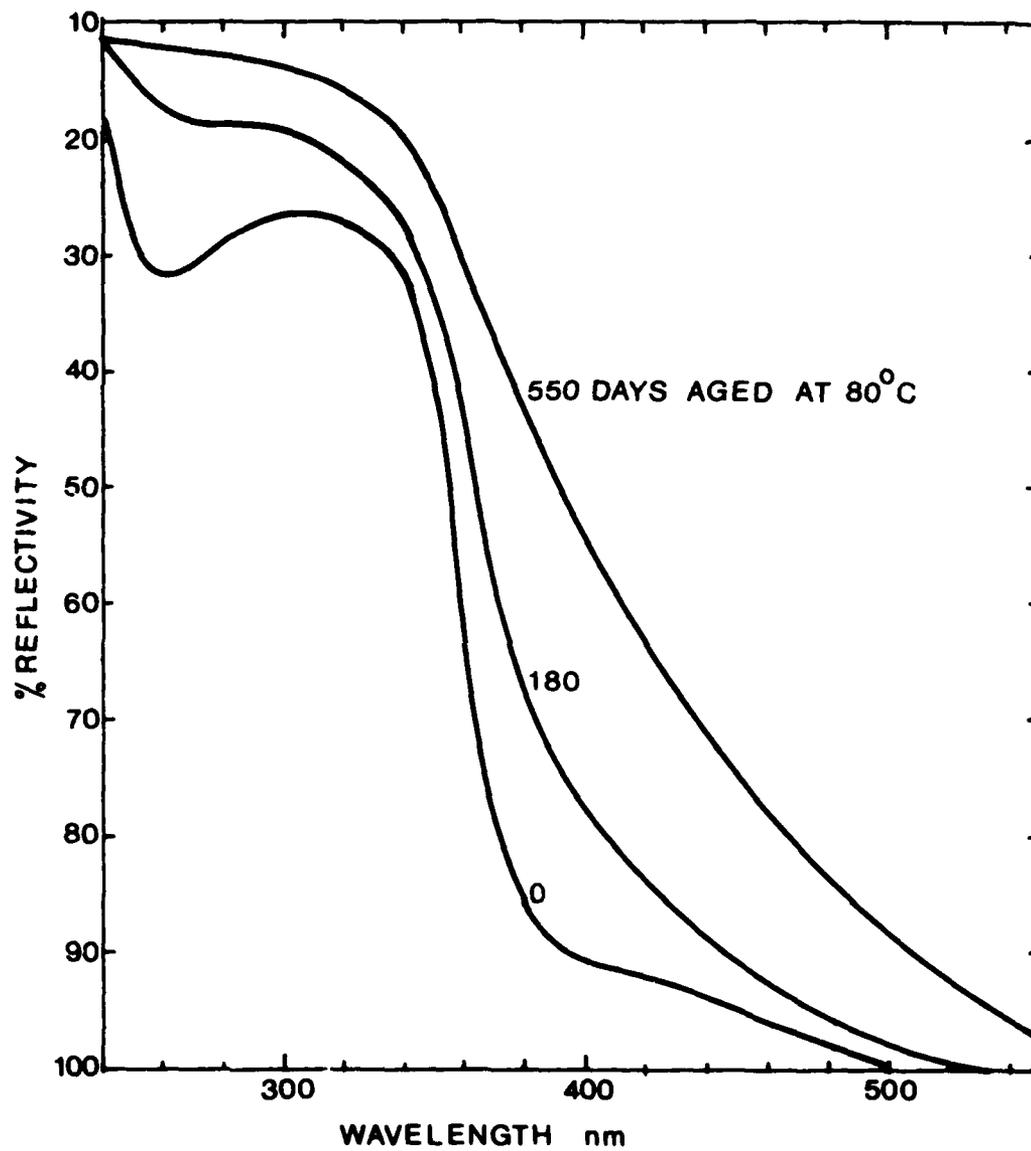


FIG. 7 - Diffuse reflectance spectra of nylon 6,6 taffeta aged at 80°C for the time shown.

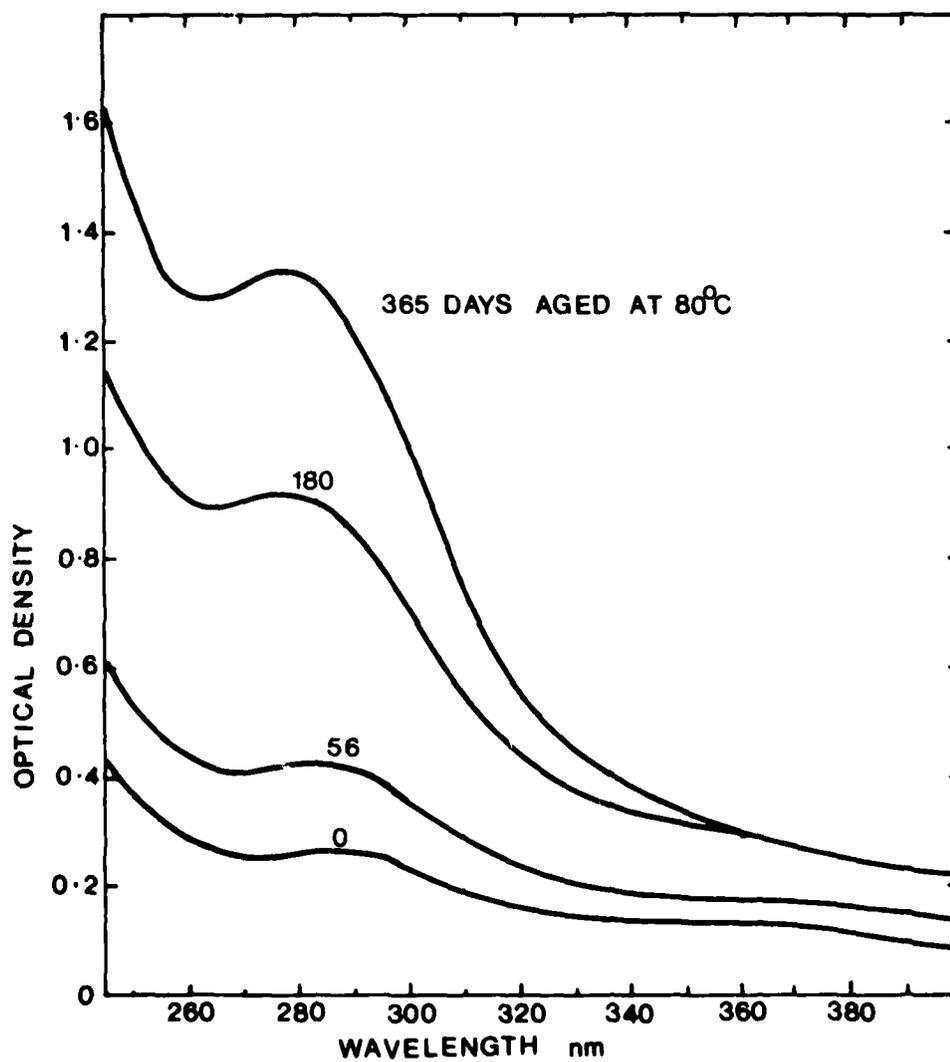


FIG. 8 - UV absorption spectrum of a 1g/dl solution in Methanol:HCl of nylon 6,6 taffeta aged at 80°C for the time shown.

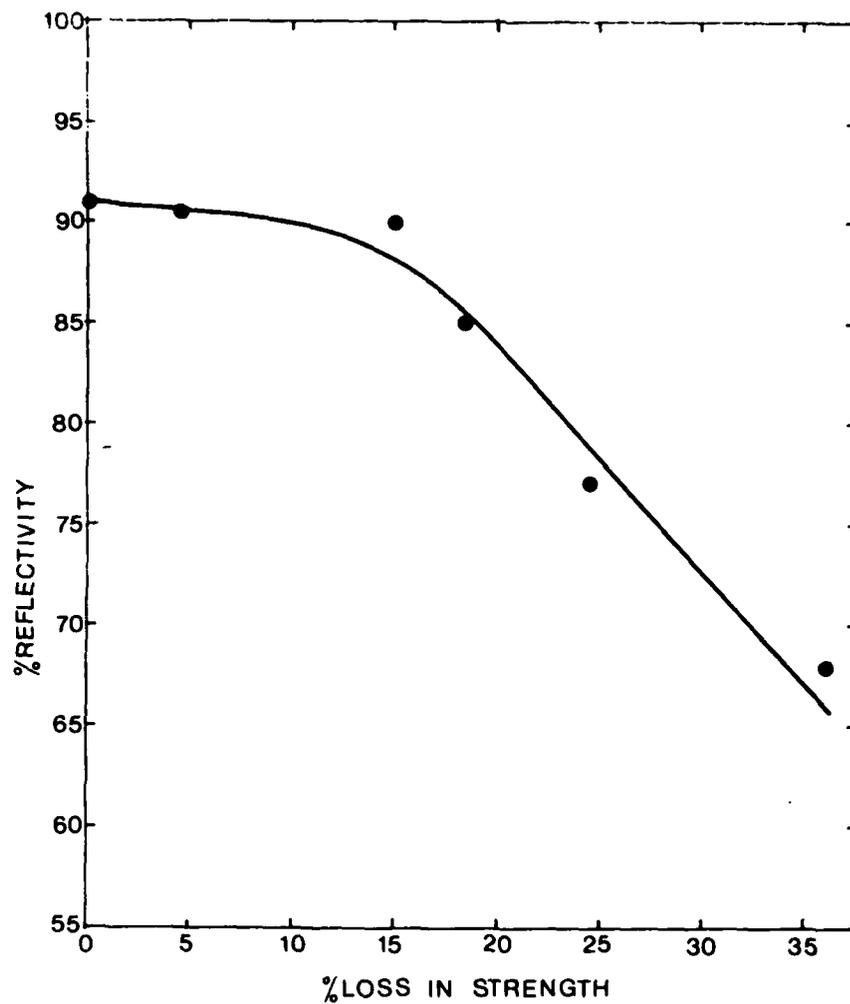


FIG. 9 - The relation between loss of strength on ageing and the % reflectivity at 400 nm of nylon 6,6 taffeta.

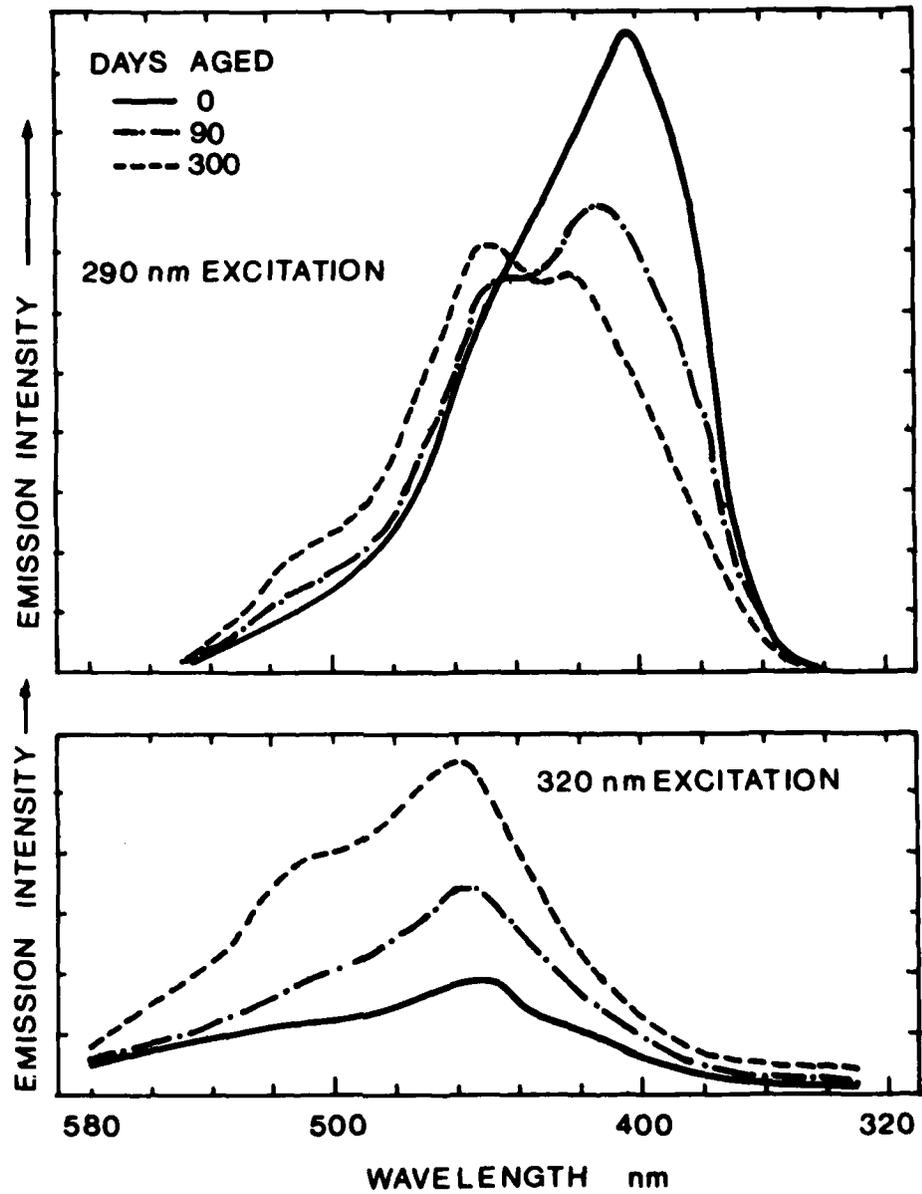


FIG. 10 - Phosphorescence spectra of nylon 6,6 taffeta on excitation at 290 nm and 320 nm.

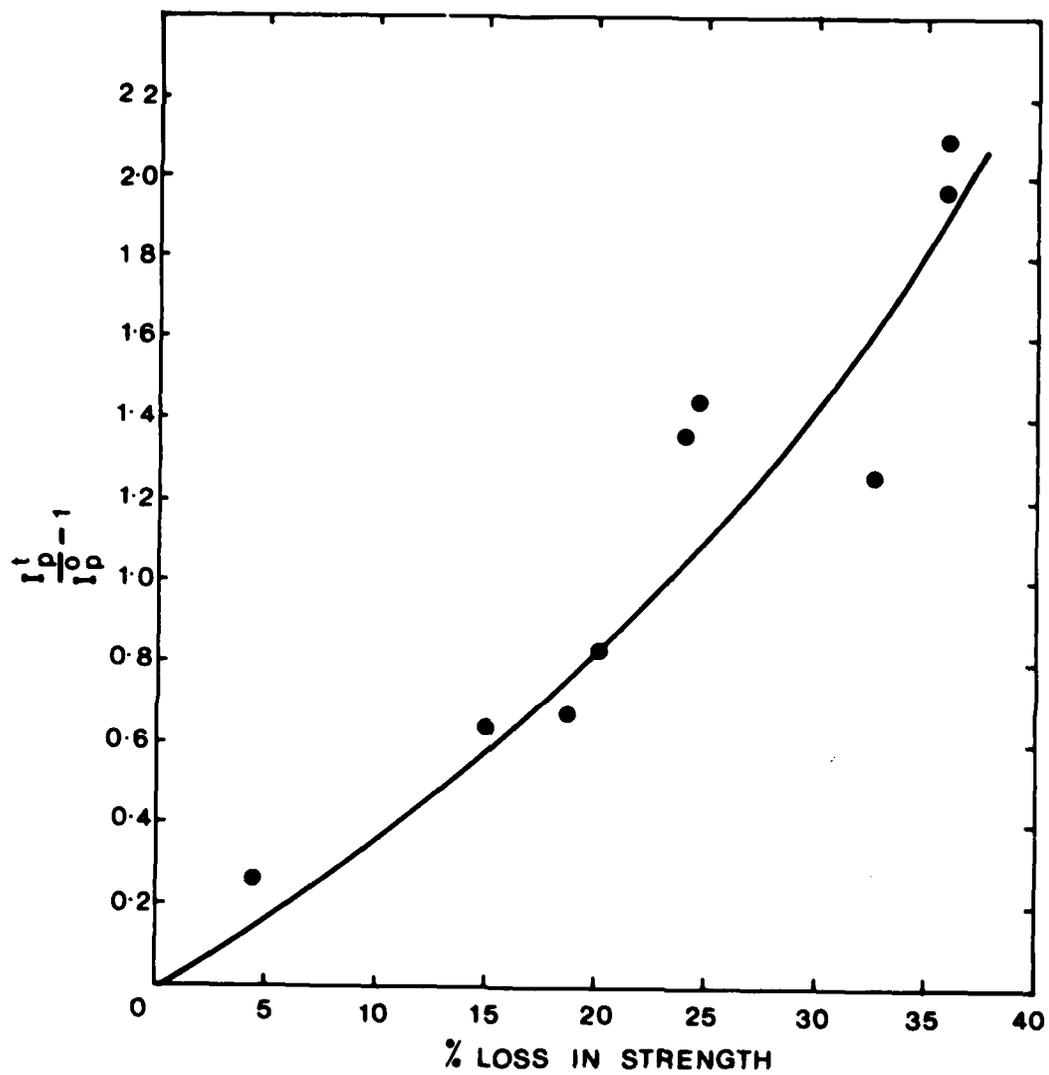


FIG. 11 - Relation between loss of strength on ageing and phosphorescence emission index ($\frac{I_p^t}{I_p^o} - 1$) of nylon 6,6 taffeta. Excitation at 290 nm and 180° observation.

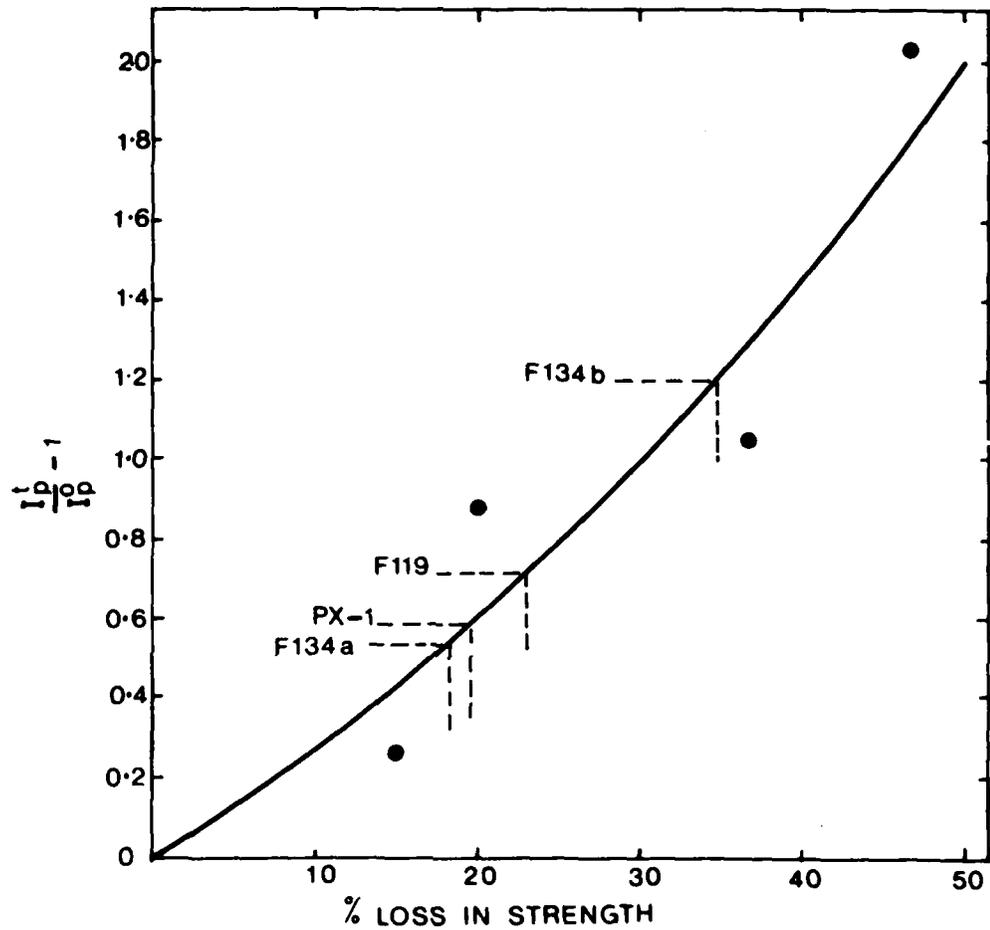


FIG. 12 - Relation between loss of strength on ageing and phosphorescence emission index ($I_p^t / I_p^o - 1$) of nylon 6,6 taffeta. Excitation at 320 nm and 45° observation. The index measured for PX-1 personnel parachutes and PB-1 free fall parachutes F119 and F134 (a: undamaged; b: damaged) is indicated.

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