

# Monitoring of Degradation of Thermally Aged Nylon 6,6. II. Pyrolysis-Gas Chromatography\*

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## Synopsis

Pyrolysis-gas chromatography was used as an analytical method to evaluate the extent of chemical changes that occur in aged yarns and to demonstrate any correlation between measured physical properties and pyrolysis products. Nylon 6,6 yarn samples (2.5–3.0 mg) that were control-degraded as a function of humidity, temperature, and time were pyrolyzed at 500°C and chromatographed on a Graphpac AT-1000 column. The peak heights of pyrolysis products unique to the degraded material were correlated with measured tensile strength loss (–5 to –75%) of the yarns. Linear relationships were found for several of the products, one of which was identified as caprolactam. Significant changes in the pyrograms were observed in nylon with tensile strength losses of 5% or less.

## INTRODUCTION

Polymeric materials, such as nylon 6,6, are often used in applications that require long lifetimes with negligible changes in the physical properties of the polymer. Exposure of these materials to environments such as humidity, elevated temperature, smog, or ozone can lead to chemical changes in the polymeric structure that may be related to changes in some physical property of the material.

Because of the stability of many polymers, the small changes in measurable physical properties that occur at room temperature over short periods of time cannot be detected or quantified well enough to have predictive value. Long-term studies at ambient temperature, although informative, may be too long to be of practical use. These shortcomings, however, may be overcome to a large extent by accelerating the aging process and developing predictive models. For a typical aging study, separate samples of material are aged at different elevated temperatures for specific periods of time. From the measured physical property changes, an Arrhenius plot can be developed for the rate dependence on temperature. The predictive models obtained from these studies assume that the chemical reactions at elevated and ambient temperatures are the same. This, however, may not be a valid assumption.

The measurement of some physical property, such as tensile strength, often leads to the complete destruction of the sample being tested. While this is an acceptable result for a control-study sample, it may be impractical or too expensive when performed on a finished product.

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TABLE I  
 Yarn Aging Conditions

Degradation (%)	Relative humidity (%)	Temp (°C)	Aging time (Days)
0 (control)	—	—	—
-5	100	90	14
-10	10	110	88
-13	50	110	88
-22	50	110	124
-26	10	130	88
-47	100	120	14
-75	10	130	124

Because the physical property changes that are observed in degraded polymers are most likely related to chemical changes, such as oxidation, hydrolysis, chain scission, or crosslinking that have occurred during the aging process, sensitive analytical techniques may provide an alternative test for physical property measurements. This is important for two reasons. First, the analytical techniques could provide greater sensitivity and precision for very small amounts of degradation, therefore minimizing the degree of extrapolation needed from aging temperatures. Second, the small amounts of material needed for the tests may not be destructive to the finished product.

Two different analytical techniques have been investigated using artificially aged nylon 6,6 yarn: pyrolysis-gas chromatography and UV-visible absorption spectrophotometry. The results of the spectrophotometric work have been reported separately.<sup>1</sup>

Although the literature contains a number of reports on the pyrolysis-GC,<sup>2-4</sup> pyrolysis-mass spectrometry,<sup>5,6</sup> and pyrolysis-GC-mass spectrometry<sup>2</sup> of nylon 6,6, all of the reported analyses were performed with undegraded nylon. No reports have been found concerning the analytical pyrolysis of degraded nylon 6,6 yarn. We report such a study here.

## EXPERIMENTAL CONDITIONS

**Materials.** The nylon 6,6 yarn obtained from E. I. DuPont de Nemours and Co. and used in this study was commercially available yarn of 210 denier, machine-twisted at 2 turns/in., and treated with a standard weaving finish.

Samples of this yarn were subjected to accelerated aging in a research program fully described elsewhere<sup>7</sup>; therefore, only a brief summary will be given here. Samples of nylon yarn were wound on glass spools and placed within stainless steel containers. The containers were placed in environmental chambers in an air atmosphere and equilibrated at ambient temperature to either 10% or 50% relative humidity (RH) before sealing. (At the elevated temperatures used for the aging study, the RH in these containers would be considerably lower.) For 100% RH samples, vials containing excess water were placed within the containers before they were sealed. Samples were aged at elevated temperatures for specific periods of time.

The tensile strength of each yarn sample was measured before and after

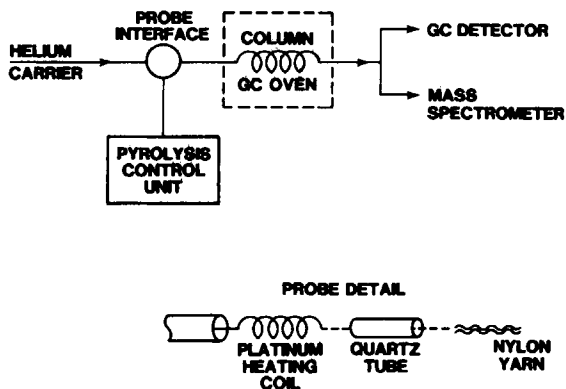


Fig. 1. Schematic diagram of instrumentation.

spooling, and again after the aging process was completed, using an Instron <sup>TM</sup> tensile tester. Table I lists the aging conditions and resulting tensile strength loss for each sample. Tensile strength loss (degradation) is defined as the percent differences of the aged nylon to an unaged control sample.

**Pyrolysis-Gas Chromatographic Conditions.** A CDS Model 120 pyrolyzer equipped with a coil-type pyrolysis probe was interfaced directly to a Varian 3711 gas chromatograph (Fig. 1). The samples (2.5–3.0 mg) were heated at 20°C/msec from ambient temperature to 500°C, which was held for 5 s. The volatile pyrolysis products were separated using a 1.8 m long, 2 mm I.D. glass column packed with 80/100 mesh Graphpac AT1000 (Alltech Associates) and programmed from 50°C to 220°C at 8°C/min. A helium carrier was used at a flow rate of 30 cm<sup>3</sup>/min. A flame ionization detector (10.E-11 AFS/mv sensitivity) and Varian CDS 111 integrator were used for peak detection and quantitation. Total analysis time per sample was 30 min.

**Pyrolysis-GC-Mass Spectrometer Conditions.** The GC-mass spectrometer employed for these analyses was a Finnigan MAT Model 112-S equipped with an SS-200 data system and Varian 3700 GC. Pyrolysis and chromatographic conditions were the same as described previously. For each analysis, the mass spectrometer was operated in a continuous scanning mode: 10–500 AMU at 2 s/decade scan rate. Resolution was set at approximately 600 (10% valley definition).

## RESULTS AND DISCUSSION

Typical pyrolysis chromatograms (pyrograms) for the control sample compared to yarn samples having –10%, –47%, and –75% tensile strength loss are shown in Figure 2. The pyrograms for the other samples (–5%, –13%, –22%, and –26%) show similar trends in products. Strip-chart attenuation was ×64 for all analyses (changed to ×256 only for the cyclopentanone peak). The pyrograms shown in Figure 2 show that both the concentrations and the observable number of pyrolysis products increase as a function of tensile strength loss. This increase in product area with degradation is shown graphically in Figure 3.

Mass spectrometry was used to examine the major pyrolysis products from

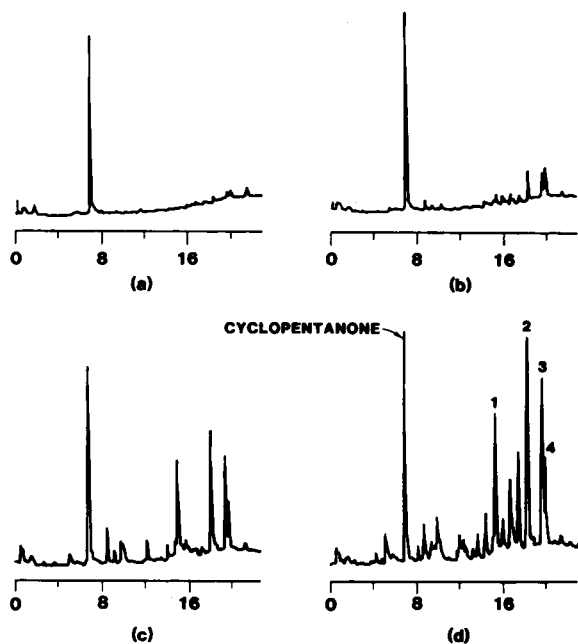


Fig. 2. Representative nylon 6,6 pyrograms: (a) control sample; (b) -10% loss; (c) -47% loss; (d) -75% loss.

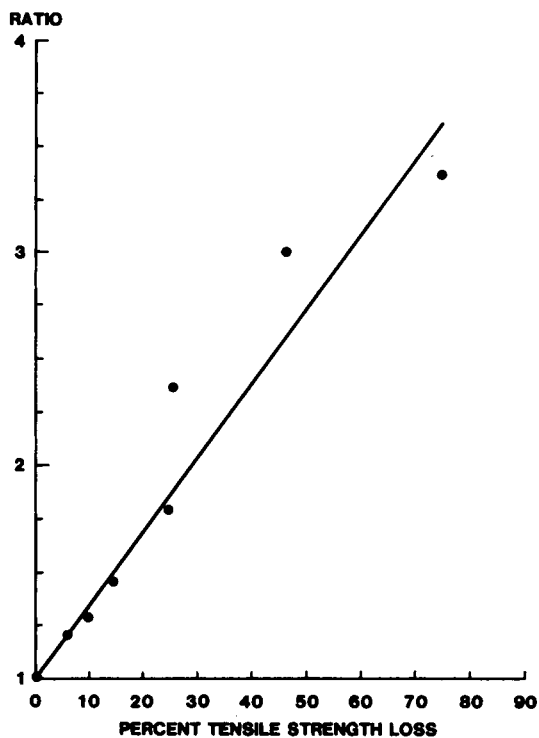


Fig. 3. Ratio of pyrogram total area to control sample area vs. percent tensile strength loss (total area is the sum of all peaks from time 0-25 min).

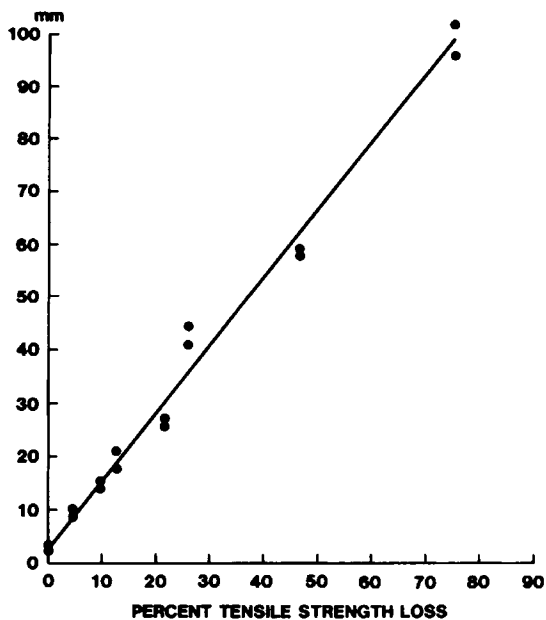


Fig. 4. Peak height vs. percent tensile strength loss for peak 2 (*N*-ethyl succinimide).

several different degraded samples. The most intense peak present in all the samples is cyclopentanone. This product, which has been reported elsewhere,<sup>8</sup> results from the decomposition of the adipic acid fractions in the polymer chain. Visual comparisons and computer library searches of fragmentation patterns

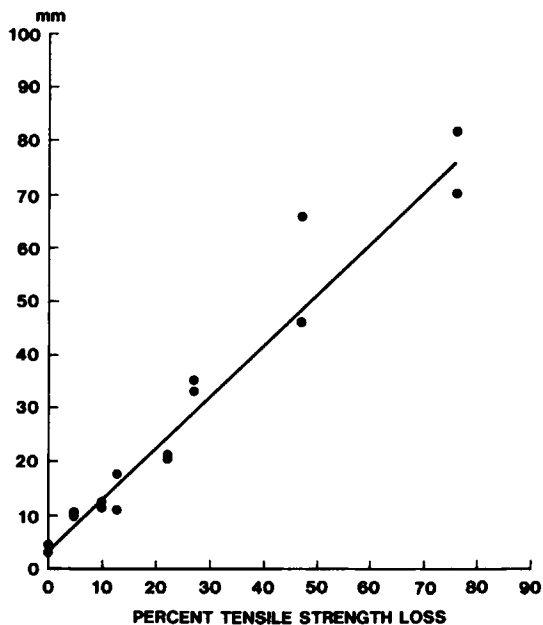


Fig. 5. Peak height vs. percent tensile strength loss for peak 3 (caprolactam).

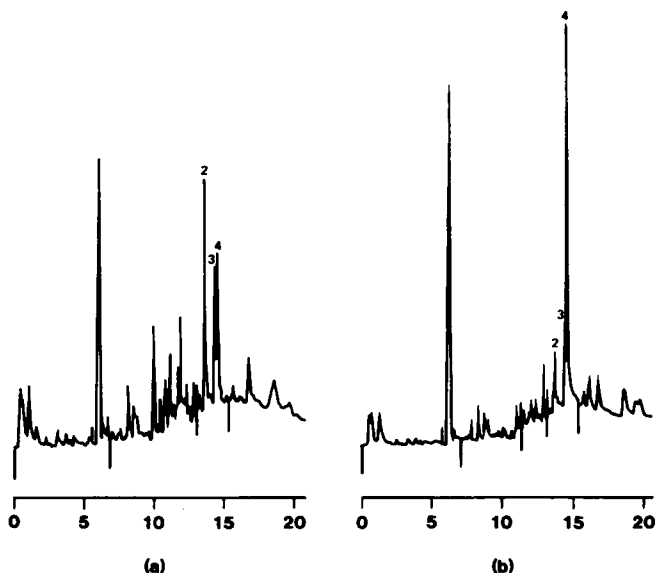


Fig. 6. Typical pyrograms for nylon 6,6 exposed to smog and ozone: (a) 6 months smog, -63% loss; (b) 6 months ozone, -4% loss.

have tentatively identified peaks 1 and 2 as adiponitrile and *N*-ethyl succinimide, respectively. Adiponitrile has recently been reported by Tsuge.<sup>2</sup> Peak 3 is a composite of two compounds, caprolactam and an apparent homolog. Caprolactam was identified by both fragmentation pattern and GC retention time. Tsuge<sup>2</sup> has also reported the presence of minor amounts of caprolactam from the 550°C pyrolysis of undegraded nylon 6,6, 6,9, 6,10, and 6,12. In contrast, he did not report caprolactam as a pyrolysis product from nylon 12,6, 12,10, or 12,12.

Plots were made of either the peak heights or the areas of all the major and of some of the minor peaks vs. tensile strength loss. At the attenuation used for these analyses, most of the minor peaks could not be measured precisely enough to produce meaningful plots. The most intense peaks, however, were of more interest as they would provide the most sensitive indicators of tensile strength loss. The results for peaks 2 and 3 (denoted in Fig. 2) are shown in Figures 4 and 5, respectively. These results are uncorrected for sample weight.

Data shown in Figures 4 and 5 were correlated, using linear regression analysis. Correlation coefficients were 0.97 and 0.95, respectively. Examination of these two plots shows that peak 2 (*N*-ethyl succinimide) would be the most sensitive indicator of thermal degradation and that tensile strength losses of 5% or less could be detected by pyrolysis-GC.

## CONCLUSIONS

Nylon 6,6 yarn aged as a function of temperature and humidity was analyzed using pyrolysis-gas chromatography. Product peak height and tensile strength loss were found to correlated linearly for at least two of the pyrolysis products examined. The correlation plots demonstrate that small physical property changes, such as tensile strength, can be detected and quantified.

## APPENDIX

Samples of nylon 6,6 yarn were also aged in smog and ozone atmospheres. The complete aging procedure is also described in Ref. 7. For these aging studies, glass spools wound with yarn were placed in a chamber maintained at 40°C and exposed to either smog or ozone for time periods up to 6 months. Spools were removed at regular intervals for yarn tensile strength measurements.

Smog and ozone degraded yarn samples were analyzed using the same conditions described for the thermally degraded samples. The Graphpac AT1000 column, however, was temperature programmed as follows: 50–75°C at 5°C/min; 75–220°C at 15°C/min. These program changes resulted in shorter retention times with no apparent loss in resolution.

**Smog Samples.** Samples of nylon 6,6 exposed to smog at 40°C showed an increasing loss in tensile strength with time of exposure. A pyrogram from a sample exposed for six months (–63% tensile strength loss) is shown in Figure 6(a). Although mass spectral analysis has not yet been completed for the smog samples, the similarity of the pyrograms for the temperature and smog degraded samples (peaks 2 and 3) suggests that the chemical structures, prior to pyrolysis, are similar.

**Ozone Samples.** Samples of nylon 6,6 yarn that were exposed to ozone for 6 months at 40°C showed little or no tensile strength loss. A pyrogram of a sample exposed for six months (–4% tensile strength loss) is shown in Figure 6(b). The peak height of peak 2 (*N*-ethyl succinimide), which has been shown to be a sensitive indicator, confirms a tensile strength loss of less than 5%. On the other hand, peak 4 (which showed no tensile strength correlation in the thermally degraded samples) increases markedly with ozone exposure. As this peak has not yet been identified, conclusions concerning its origin cannot be drawn.

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