

# Monitoring of Degradation in Thermally Aged Nylon 6,6. I. UV-Visible Absorption Spectrophotometry\*

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## Synopsis

The absorbance of chromophores developed upon thermal aging of a typical nylon 6,6 yarn is investigated. The absorbance is found to correlate with the degree of tensile strength loss suffered by the yarn during the aging process. The measurement is shown to be quite sensitive, as the absorbance from samples with levels of strength loss as low as 5% has been monitored. It is predicted that similar samples with only 1–2% tensile strength loss should be distinguishable from control samples using this technique. Implications for the monitoring of aging at ambient temperatures are discussed.

## INTRODUCTION

All polymers, even while in the solid state, undergo chemical reactions such as chain scission, crosslinking, oxidation, hydrolysis, etc. While these reactions are usually quite slow under ambient conditions, their cumulative effect over a long (years) period of time is a degradation in bulk physical properties, such as tensile strength or elasticity. The measurement of the extremely small changes in bulk properties, such as tensile strength, which occur at room temperature over relatively short experimental times (e.g., a few months) is difficult to accomplish with good precision. In addition, many of the bulk measurements require testing to sample failure, which lessens the attractiveness of the measurement for large-scale testing, as in quality control.

Currently, the effective useful lifetime of polymeric materials is usually determined by accelerated aging techniques. In such tests, separate samples of the material of interest are aged at a series of elevated temperatures. In this way, measurable changes in bulk properties can be achieved fairly quickly. The temperature dependence of the rate of change in the properties (usually expressed as an Arrhenius plot) can then be determined, and an extrapolation to ambient temperature made. In performing such a test, one must assume that the reactions which are important to degradation of bulk properties at elevated temperatures are the same reactions which are important at ambient temperatures. This assumption may or may not be justified.

One would like to find a property whose changes correlate with changes in the bulk property of interest, and which can also be measured with very good sensitivity and precision. One might then be able to monitor changes in the sensitive property which correspond to changes in the bulk property that are too small

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to measure directly. It could then be possible to monitor aging which occurs over shorter times and/or at lower temperatures.

In pursuit of this goal, we have made two types of measurements, pyrolysis-GC and UV-visible absorption spectrophotometry, on artificially aged samples of nylon 6,6. The results of the pyrolysis work are outlined in a separate report.<sup>1</sup>

A number of authors have studied the chemical and physical changes which occur upon UV irradiation of nylon 6,6.<sup>2-9</sup> Of these, several have monitored UV-visible absorption spectra as a function of irradiation time or changes in bulk properties.<sup>7-9</sup> Allen et al.<sup>5</sup> studied the formation of phosphorescent species both after thermal oxidation and photooxidation. Several other authors have reported studies of aging of nylon 6,6 under thermooxidative conditions.<sup>10-12</sup> In addition, a number of peaks in the second-order derivative UV absorbance spectrum of unaged nylon 6,6 have been reported.<sup>13</sup> However, we know of no studies in which the absorption spectra of nylons have been correlated with changes in bulk properties for samples aged without UV irradiation. We report such a study here.

## EXPERIMENTAL

A number of nylon samples were aged at elevated temperatures for different lengths of time to produce a range of tensile strength losses. A complete description of the aging procedure has been previously reported.<sup>12</sup> Therefore, only a summary of the procedure will be repeated here.

The nylon 6,6 samples consisted of 210-denier yarn obtained from E. I. DuPont de Nemours and Co., machine twisted at two turns per inch, and treated with standard weaving finishes. A yarn sample was analyzed using DC arc emission spectrometry and found not to contain significant levels of Ti, Mn, or Cu (<50 ppm in each case). The material was chosen to be representative of the yarns usually employed in parachute construction, the aging of which is of wide interest. Samples were aged by winding the yarn on glass spools and sealing the spools inside stainless steel tubing at constant temperature. The tensile strengths of the unaged yarns were determined using an Instron TM tensile tester. These tests were run both before and after winding on the spools to ensure that the winding process did not affect the tensile strength. Tensile strengths were measured again after aging. Aging conditions and resulting tensile strength losses for the samples employed in the current study are shown in Table I.

TABLE I  
Yarn Aging Conditions

Relative humidity <sup>a</sup> (%)	Temp (°C)	Aging time (days)	Tensile strength loss (%)
—	—	—	0 (control)
100	90	14	5
10	110	88	10
10	130	88	26
10	130	124	75

<sup>a</sup> See text concerning measurement of relative humidity.

Samples listed as having 10% RH were equilibrated at room temperature, sealed, and raised to the aging temperature. The RH at the elevated temperature would, of course, be lower than 10% (<0.5% in each case). For samples with 100% RH, vials of water were placed in the sealed canister to ensure that the RH would be 100% at any temperature.

UV-visible absorption spectra were run using a Cary 17 Spectrophotometer. Aged yarn samples were dissolved in 2,2,2-trichloroethanol, 98%, obtained from Aldrich Chemical Co. and used as received. Higher effective concentrations of chromophores could have been obtained by taking spectra of nylon in the solid phase. However, this would require casting the yarn in a film, either before or after aging, and this process might alter the type or measured rate of the aging reactions. Spectra were run in 1-cm matched quartz cells. For each series of spectra recorded, at least one blank spectrum was first run using pure solvent in both sample and reference cells to provide correction for any nonzero baseline.

Diffuse reflectance and photoacoustic spectroscopies could in principle be used to obtain similar spectra without the need to dissolve the samples. However, other problems would have to be overcome in the use of these methods, especially regarding sample preparation.

## RESULTS AND DISCUSSION

The nylon samples developed a visible coloration which seemed to correspond to the degree of aging. Samples ranged from colorless for the control sample to slightly yellow for the lightly degraded samples to brown for the samples with 75% strength loss. Therefore, it seemed reasonable that a correlation between strength loss and UV-visible absorbance could be established. Typical spectra for several of the samples are shown in Figure 1. The spectra are uncorrected for the blank, which is  $-0.025$  absorbance units at the wavelength of maximum absorbance. It should be noted that the downward slope of the spectra when scanning to wavelengths below ca. 245 nm is an instrumental artifact due to the large absorbance of the solvent in that region. The trichloroethanol solvent has an absorbance  $\gg 2$  at 240 nm, which is difficult to subtract from the sample absorbance.

Most of the solvents which dissolve nylon 6,6 are acids and could conceivably hydrolyze the chromophores of interest. Trichloroethanol was used to minimize this possibility. In order to determine if solution phase reactions were altering the measured absorbances, measurements were taken with samples that had been dissolved for a few hours, about 1 day, and about 2 days. No differences in the measured absorbances were observed.

Similar absorption spectra were observed upon photooxidation of poly(*n*-butyl acrylate).<sup>14</sup> In that case, the increase in absorption was attributed to the formation of small molecular weight fragments, such as 1-butene. Thermal oxidation of polyamides and model amide systems have been shown to involve the formation and propagation of peroxides,<sup>7,15,16</sup> leading to the formation of ketonic and aldehydic carbonyls and alkenes. Allen et al.<sup>5</sup> observed phosphorescence from oxidation products in nylon 6,6 which they identified as  $\alpha,\beta$  unsaturated carbonyls. The exact nature of the absorbing species here is unknown, and further studies on this problem are ongoing. However, the analytical utility of

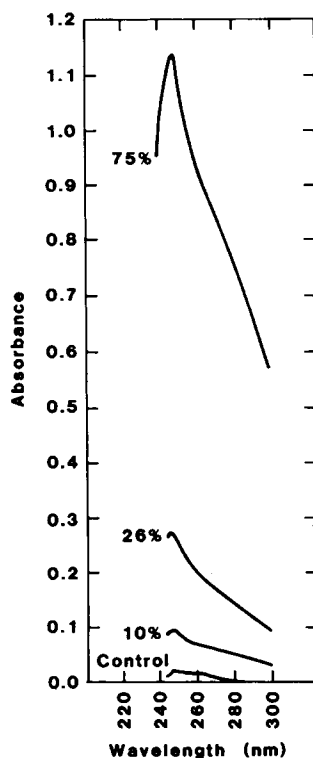


Fig. 1. Absorbance spectra of aged yarn samples dissolved in 2,2,2-trichloroethanol. Tensile strength loss of each yarn is listed beside its spectrum. Concentrations are 1.42 mg/mL.

the method rests on a reproducible correlation of absorbance with tensile strength loss. Such a correlation is shown in Figure 2, where the maximum absorbance developed is plotted against the measured tensile strength loss for 1.42 mg/mL solutions of aged and control yarns. The wavelength of maximum absorbance was nominally 245 nm, but this varied by ca. 1 nm in some cases due to slight differences in the absorbance developed by solvent from different bottles. A datum from a yarn sample aged for 14 days at 120°C and 100% relative humidity was also taken. The datum fell below the curve drawn (0.19 absorbance units), but was not plotted since the tensile strength loss could not be well characterized, ranging from 39% to 54%. Apparently, this particular sample did not age uniformly.

In order to insure that the absorbance which developed was the result of nylon aging and not discoloration of a finish or additive, samples of pure nylon were also aged. Nylon 6,6 with no additives of any kind (Celanese N-208) was extruded into 0.010 in. diameter monofilaments by E.B. and A.C. Whiting Co. (Burlington, Vt.). No finish or surface treatment was applied. After aging under similar conditions as the yarns (130°C, 70% RH), the same yellow discoloration and UV absorption was observed to develop. In addition, the observed correlation between tensile strength loss and signal from a different analytical technique, pyrolysis-GC, further confirms that the observed signal originates in degradation of nylon itself.<sup>1</sup>

The curve which best fits the data points displays an increasing slope in going

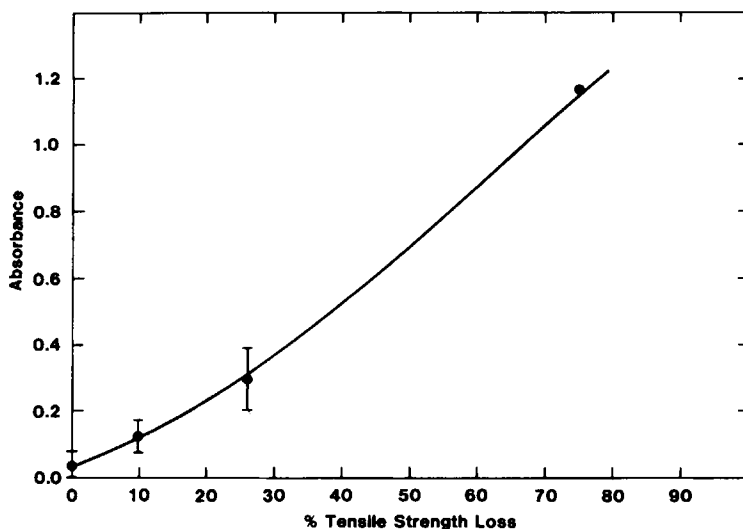


Fig. 2. Maximum absorbance of 1.42 mg/mL solutions of aged yarns vs. tensile strength loss. Error bars are  $\pm$  two standard deviations.

from the low loss to high loss side of the ordinate. It has been shown<sup>17</sup> that properties such as tensile strength, which depend on the number of ends of polymer chains, obey the relation

$$\text{property} = a - b/\overline{M}_n$$

where  $a$  and  $b$  are constants and  $\overline{M}_n$  is the number-average molecular weight. If the number of chromophores formed during degradation is proportional to the number of chain scissions, a similar relationship should exist between the absorbance developed and  $\overline{M}_n$ . Under these conditions, the absorbance would vary linearly with tensile strength loss. A more complex mechanism is operative here, possibly involving chain scission followed by intermediate steps prior to chromophore formation or a depth-dependent degradation. A similar correlation was observed by Moore for the photodegradation of delustered nylon 6,6 yarn.<sup>8</sup> More data are needed to elucidate the mechanism involved, but the relationship is analytically useful since it is reproducible, smooth, and monotonic.

It is interesting to note that the control yarn had a nonzero absorbance. This is consistent with earlier reports of so-called impurity chromophores present in unaged nylon and assumed to be formed during synthesis or processing.<sup>5,18</sup> However, much of the absorbance from the control yarn may be due to room temperature aging, as it was more than 4 years old when tested.

The ultimate aim of this work was to demonstrate the feasibility of quantifying degradation at very low levels. In order to accomplish this, a higher absorbance was needed for the yarns exhibiting low strength loss. The simplest way to develop a stronger absorbance signal from any given sample is to make the solution more concentrated. One would hope that Beer's law would be obeyed, i.e., a more concentrated solution would give a proportionally higher absorbance. A Beer's law plot for several concentrations of yarn with 10% strength loss is shown in Figure 3. Clearly, Beer's law is obeyed at 245 nm over the limited range of concentrations studied. At higher concentrations, one might expect interaction

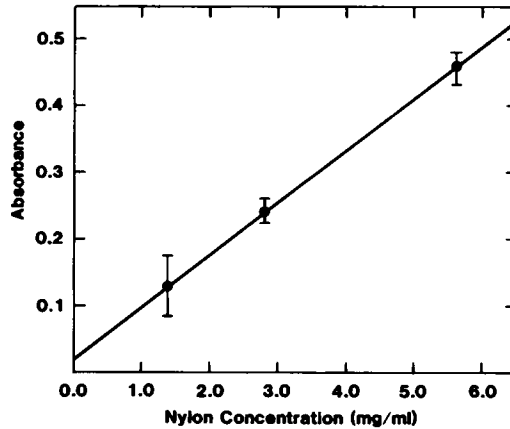


Fig. 3. Maximum absorbance of nylon yarn solutions vs. nylon concentration for yarns with 10% tensile strength loss. Error bars are  $\pm$  two standard deviations.

of the polymer chains to cause nonlinearities. Of course, the polymer solubility would provide the ultimate limit on the maximum possible absorbance for a given path length.

Using the maximum concentration employed in the Beer's law plot (5.62 mg/mL), spectra were run of the control, 5%, and 10% strength loss samples. Absorbance data are shown in Figure 4. Two features of this plot are noteworthy. First, the shape of the curve is very similar to the shape of the curve in Figure 2. Second, the difference in average absorbance between the control sample and the sample with 5% strength loss was substantial, 0.124 absorbance units. At the level of precision obtained for these data, the absorbance measurement can readily distinguish between the control and 5% strength loss samples. By interpolating between these measured points, one finds the method should be sufficiently precise so as to distinguish between a control sample and an aged sample with degradation corresponding to 1% or 2% strength loss. Such low levels of degradation might be observed with ambient or slightly elevated tem-

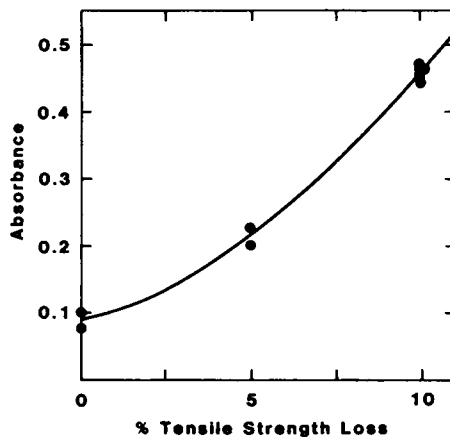


Fig. 4. Maximum absorbance of 5.62 mg/mL solutions of aged yarns vs. tensile strength loss.

perature aging. A number of samples with very low levels of degradation are now being prepared to test this idea.

Since aging of the polymer itself is producing the observed signal, the technique should be applicable to aging studies of other formulations of nylon 6,6. However, it should first be demonstrated that the formulation of interest has no potential interferents, e.g., a dye which absorbs strongly in the 245 nm wavelength region. One should expect that for a given set of aging conditions the rate of formation of chromophores and possibly the specific form of the absorbance vs. tensile strength loss curve would be a function of the additives employed. The aging studies described here should therefore be repeated when beginning the study of other nylon formulations.

Since only milligram quantities of material need be dissolved for this type of analysis, the technique might also be useful in quality assurance applications.

## CONCLUSIONS

Solutions of thermally aged nylon 6,6 yarn have been found to exhibit an absorbance at 245 nm. The strength of the absorption is shown to correlate with the degree of tensile strength loss in the aged yarns. Beer's Law is obeyed at least up to a concentration of 5.62 mg/ml for a yarn with 10% strength loss. The observed absorbance is shown to originate in the polymer itself, rather than as the result of discoloration of an additive or finish. Using only milligram quantities of material, the sensitivity and precision of the method should allow the monitoring of degradation of the formulation used at the 1–2% strength loss level.

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