Photodegradation of Nylon 66.   I.
Phototendering by TiO$_2$

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Synopsis

The mechanism by which TiO$_2$ exerts a phototendering effect on nylon 66 photodegradation has not been previously explained.   To aid in the elucidation of this mechanism, the wavelength dependence curves of photodegradation of nylon 66 both with and without TiO$_2$ have been accurately determined.   These data, in conjunction with reflectance and phosphorescence measurements, indicate that the phototendering effect of TiO$_2$ proceeds by a chemical rather than an energy transfer mechanism.

INTRODUCTION

The loss in properties of nylon 66 on exposure to radiation in the near-ultraviolet region has been the subject of a number of papers over the past ten years.[1-15]   The quantity of work on nylon 66 attests to the commercial significance of this polymer and the importance of its light stability in practical applications.   Most of the previous work has been concerned with the reactions that occur after formation of a free radical by the initial absorption of energy.   This initial absorption and the step or steps leading to the production of the first free radical have been subject to much less detailed study.   These subjects have been the object of the present work.

A number of empirical observations has been reported in the course of research on nylon 66 photodegradation which have not been satisfactorily explained.   A number of workers[4,5,6,10] have reported that TiO$_2$ greatly increases the rate of photodegradation of nylon 66.   A wide range of possible suggestions for the mechanism of TiO$_2$ phototendering has been proposed.   However, critical experiments for deciding between these mechanisms have not been reported.

At least three possible roles can be suggested for the phototendering effect of TiO$_2$ in nylon 66:   the TiO$_2$ may be involved in the free radical–peroxide degradation mechanism[6]; TiO$_2$ may produce peroxides itself when exposed to light in the presence of oxygen and/or moisture[9]; and TiO$_2$ may sensitize degradation by transfer of energy to the nylon matrix by one of the well-known energy transfer mechanisms.[14-16]   If either mechanism 2 or 3 is operative, the wavelength dependence of nylon 66 photodegrada-

tion should be altered by addition of TiO_2.   However, mechanism 1 should not alter the wavelength dependence.   Differentiation between mechanisms 2 and 3 can be accomplished from luminescence spectra of nylon 66.

EXPERIMENTAL

The nylon samples used in this work were commercial 40-denier, 13-filament textile yarns manufactured by Monsanto's Textiles Division.   None of the samples contained stabilizers of any kind.   The bright and dull yarns contained 0% and 2.0% anatase TiO_2 (du Pont LOCR type TiO_2), respectively.

Numerous reports on the wavelength dependence of nylon 66 degradation have appeared.   These studies all indicate that absorption of radiation below 3000 Å leads to nylon degradation.   Most of these studies have involved exposure behind filters to select the desired wavelengths.   Unfortunately this procedure does not permit accurate determinations of the wavelengths causing degradation and does not permit detection of small differences between samples.

A technique for wavelength dependence studies which is similar to a technique previously reported by Hirt et al.[17] has been developed and used for this investigation.   This technique makes use of a high dispersion spectrograph for accurate wavelength selection and permits a complete wavelength dependence curve to be obtained from a single exposure.   The source for these studies was a 900-watt Hanovia high-pressure xenon arc lamp having an energy distribution with wavelength similar to that of sunlight.   The light from the source was focused with a quartz 6.3-cm lens onto the slit of a Jarrell-Ash Model 7500 $^3/_4$ m grating spectrograph. This unit was selected because of its very high light-gathering power (f 6.5).   It is equipped with a 5,000 line-per-in. grating (blazed at 3000 Å) and has a dispersion of approximately 20 Å per mm (1st order) at the plate holder.   The camera accommodates 5 × 7-in. plates so that in one exposure a wavelength range of from 2000 Å to 5500 Å can be covered.   The camera was calibrated with a low pressure mercury arc.

Polymer films can be placed directly in the plate holder and exposed or samples can be ultimately fiber-taped to a photographic plate perpendicular to the dispersed spectrum.   The wavelength striking any point of the fiber could be determined to within ± 10 Å.   The extent of degradation was determined for fiber by measuring the loss in tensile properties on an Instron tensile tester.   The high dispersion of the spectrograph gave quite low intensities at any given wavelength, so that relatively long exposures of the order of hundreds of hours were required for meaningful changes in physical properties.

Reflectance spectra were obtained using an apparatus set up in this laboratory expressly for this work.   The output from a 150-watt dc xenon arc was focused on the entrance port of a 3-in. reflectance sphere attachment for a Beckman Model B spectrophotometer.   The sphere was coated

with smoked MgO.   The reflected light from the sample was dispersed with a Jarrell-Ash F/3.6 0.25 m monochromator with an R212 (1P28 Type) photomultiplier tube as detector.   The reflectance curves for the samples of interest were measured versus a smoked MgO standard.   Reflectance spectra were used instead of absorption spectra since matrix effects would be eliminated and the resulting spectra would have greater relevance to the wavelength dependence studies.

As part of this study, phosphorescence spectra of nylon 66 were also obtained.   These spectra were run on a Hitachi Model MPF-2A spectrofluorometer equipped for phosphorescence studies at 77°K.   Lifetime measurements were also made by feeding the signal from the phosphoroscope to a Tektronix storage oscilloscope and chopping the exciting light with a guillotine shutter.

RESULTS AND DISCUSSION

The wavelength dependence curve of nylon is shown in Figure 1 and of nylon with TiO_2, in Figure 2.   Reflectance curves of bright and dull nylon and TiO_2 are shown in Figure 3.   The phosphorescence excitation and emission spectra and their corresponding lifetimes for nylon 66 and nylon 66 containing TiO_2 are shown in Figures 4 and 5, respectively.
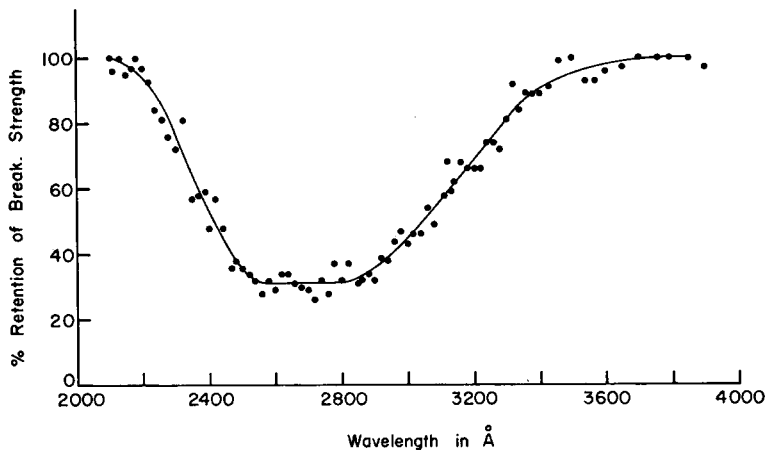

Fig. 1. Wavelength dependence of photodegradation of bright nylon 66.

A comparison of the curves shown in Figures 1 and 2 readily demonstrates that the addition of TiO_2 to nylon 66 greatly alters the wavelength dependence of degradation.   Furthermore, the shift is to longer wavelengths in the TiO_2-containing polymer, a region in which much higher intensities are present in normal sunlight.   Thus, the great increase in sensitivity to photodegradation of nylon 66 with TiO_2 can be immediately understood. The increase in strength at low wavelengths is probably due to the falloff of the source intensity in this region.
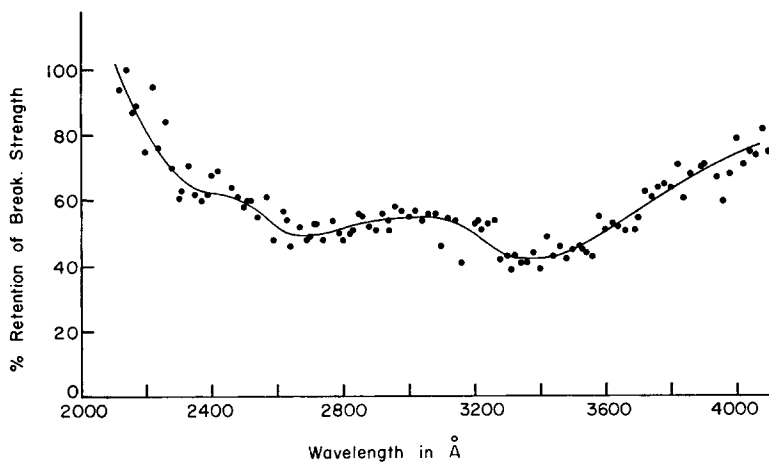
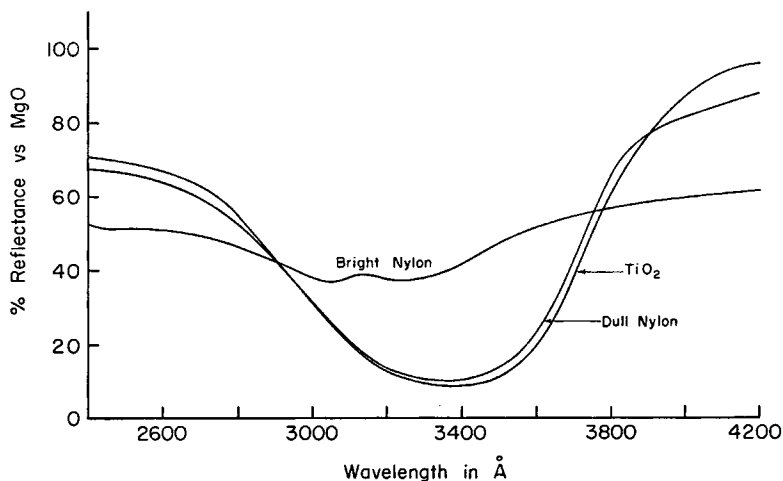Fig. 2. Wavelength dependence of photodegradation of dull nylon 66.

Fig. 3. Diffuse reflectance spectra of bright and dull nylon and TiO₂.

The reflectance spectra of TiO_2 and the two nylons are also instructive. The new degradation band in nylon 66 with TiO_2 corresponds exactly with a new absorption band on addition of TiO_2. The spectrum of TiO_2 further demonstrates that this new band is due to the TiO_2 absorption itself. The experiments clearly show that the phototendering of nylon by TiO_2 occurs through absorption of light by TiO_2 and subsequent degradation of the nylon. The mechanism of the phototendering is not, however, clear from the wavelength dependence studies alone. In this regard, the phosphorescence spectrum of nylon is of considerable interest.

Figures 4 and 5 show that nylon emits long-lived radiation at 4100 Å when excited by light of 2900 Å. It may be significant that the same wave-
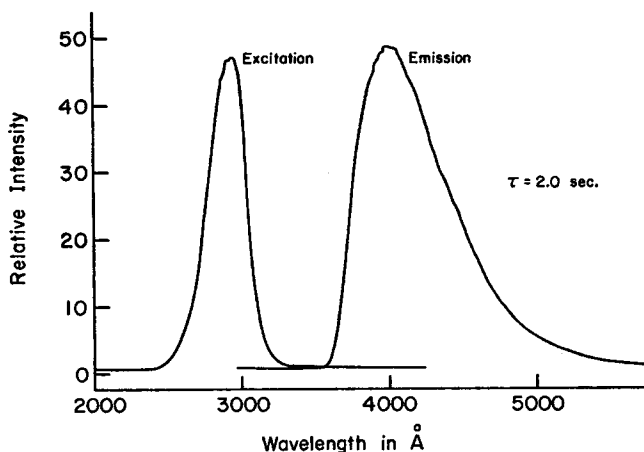
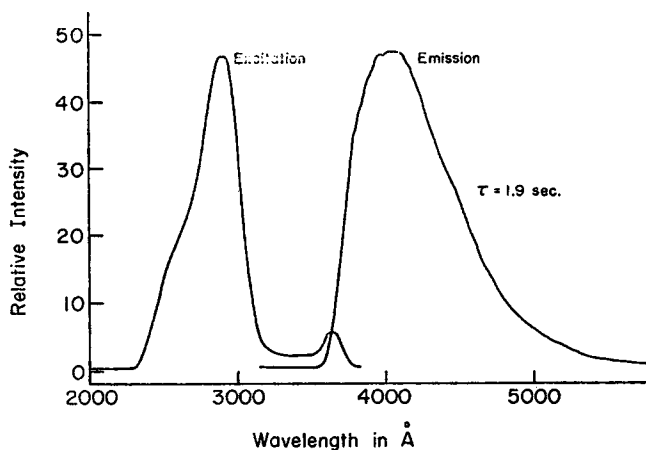Fig. 4. Phosphorescence excitation and emission spectra of bright nylon.

Fig. 5. Phosphorescence excitation and emission spectra of dull nylon.

lengths which produce degradation also populate the emitting state. The lifetime of 2 sec suggests that the emitting state is a triplet state. Thus, in normal nylon 66 energy is absorbed at 2900 Å to give nylon in an excited singlet state and by intersystem crossing a significant population of the triplet state occurs. This triplet state may be intimately connected with the nylon photodegradation mechanism.

The effect of TiO_2 on the population of this triplet energy state is of considerable importance. The fact that the TiO_2 absorption lies below the singlet state of nylon rules out the possibility of singlet–singlet energy transfer from TiO_2 to the nylon. However, absorption of light by TiO_2 to its excited singlet, intersystem crossing to the TiO_2 triplet state, and

energy transfer to the triplet state of nylon 66 cannot be ruled out by absorption studies alone.

The phosphorescence spectra in Figures 4 and 5, however, do provide some insight into this problem.   In addition to the major excitation band at 2900 Å in Figure 5, a minor band is seen at 3650 Å.   This is probably due to the TiO_2 because it does not appear in the spectrum of bright nylon (Fig. 4).   Since its magnitude is only about one tenth of that of the 2900 Å band, it does not appear to be a major contributor to the population of the triplet state.   Thus, although the possibility of triplet–triplet energy transfer may not be entirely ruled out, it does not appear to be a significant factor in the phototendering mechanism.

The results of these experiments strongly suggest that TiO_2 initiates nylon 66 degradation by absorbing radiation and producing free radicals or peroxides which can chemically attack the nylon 66.   Thus, the TiO_2 provides a new route to initiation of nylon degradation which is sensitive to light of much longer wavelengths than nylon without TiO_2.

A related problem in nylon 66 degradation is the mechanism by which manganese stabilizes nylon 66 containing TiO_2 against degradation.   This phenomenon will be the subject of a future communication.

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