Decrease in Fluorescence and Phosphorescence Intensity of Nylon 66 Impurities by Exposure to Ultraviolet Radiation

CHANDIS R. BRASINGTON* and F. GADALA-MARIA†

Department of Chemical Engineering, University of South Carolina, Swearingen Engineering Center, Columbia, South Carolina 29208

SYNOPSIS

The effects of exposure to ultraviolet radiation on the fluorescence and phosphorescence intensity of impurities in nylon 66, sometimes called gel, were measured using color image processing. The fluorescence intensity of the gel particles and of the polymer showed an approximately exponential decay with the time of exposure to ultraviolet radiation, with decay constants in the range 0.5 to 1.0 h^{-1}. Analysis of images that were acquired over several hours also indicated a decrease in the phosphorescence intensity of the gel particles. Image processing provides a simpler and less expensive method of luminescence analysis than the spectroscopic techniques used previously to examine the effects of exposure to ultraviolet radiation on the phosphorescence properties of nylon 66 impurities. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A major cause of breaks during the spinning of nylon 66 fibers is the presence of a class of impurities, called gel, in the polymer. The molecular structure of the gel and the way in which it is formed are not yet well understood. The gel exhibits fluorescence and phosphorescence when exposed to ultraviolet radiation. In a previous article[1] we showed that color image processing methods could be used to classify the impurities trapped in filters, called pack screens, by their hue under ultraviolet light into two basic groups that correspond to their hue as seen by the naked eye: "green" gel and "red" gel. Observations from our previous research indicated that as gel particles on pack screens were examined under ultraviolet light, the intensity of their fluorescence and phosphorescence emissions decreased. The present work quantifies these observations.
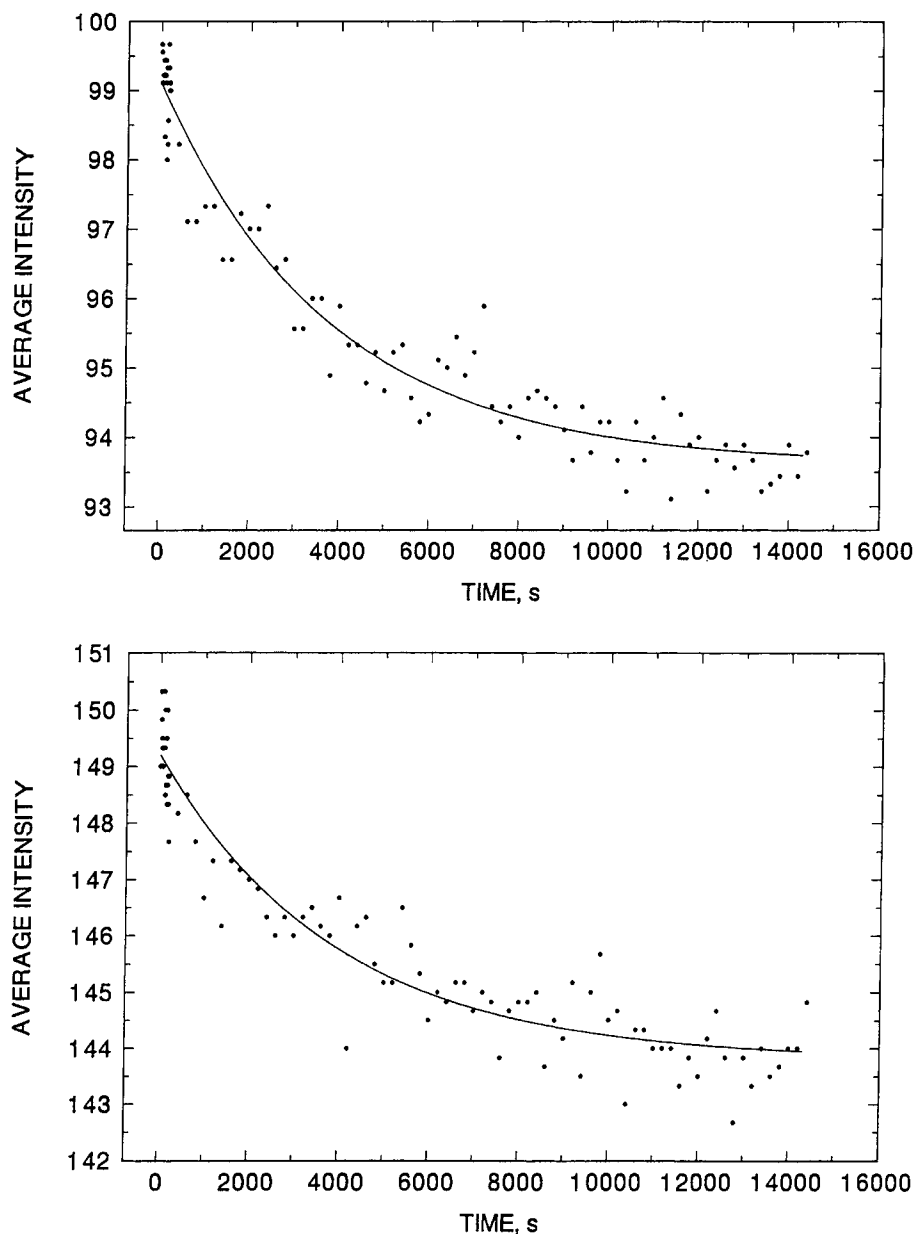
---

* Present address: Milliken & Co., Cypress Plant, Blacksburg, SC.

† To whom correspondence should be addressed.

PREVIOUS WORK

Previous investigators have examined the fluorescent and phosphorescent species in nylon 66.[2-5] Nylon 66 should not phosphoresce because neither the amide linkage, the carboxylic acid end group, nor the amine end group phosphoresce. Thus, the observed phosphorescence must be due to impurities in the polymer.[3] Dearman et al.[6] found that fluorescence was not observed in adipic acid or hexamethylenediamine (the raw materials for nylon 66), indicating that the amide group was not responsible for the fluorescence in the polymer. They concluded that the fluorescence in nylon 66 was also due to an impurity. Luminescent species in nylon 66 have been thought to result from thermal or oxidative degradation of the polymer during production.[7]

It is known that ultraviolet radiation degrades untreated nylon 66, resulting in a loss of mechanical properties and in a lowering of its molecular weight.[8] Commercially, nylon 66 is treated with manganese for protection from ultraviolet radiation.[9] In 1974, N. S. Allen et al.[3] examined the photooxidation effects on the phosphorescence properties of nylon 66 impurities. When excited by ultraviolet radiation at

Figure 1 Decrease in fluorescence intensity with length of exposure to ultraviolet light for several gel particles.

300 nm, they observed two peaks, at 425 nm and 465 nm, in the phosphorescence emissions from nylon 66. Upon photooxidation of nylon 66 at 300 nm for 140 h, the peak at 425 nm disappeared and only one emission peak at 455 nm was observed. Further photooxidation resulted in a slight decrease in the size of the emission peak. Photooxidation of nylon 66 at 280 nm did not result in any shift in the wavelength of the emission peak, but photooxidation at

320 nm resulted in a slight decrease in the wavelength of the peak. In addition, photooxidation at these three excitation wavelengths resulted in a significant decrease in both the mean lifetime and the intensity of the phosphorescence. H. A. Taylor et al.[2] studied the photodegradation of nylon 66 and showed that the same wavelengths that produce degradation of the polymer also excite the triplet state responsible for phosphorescence. We are not
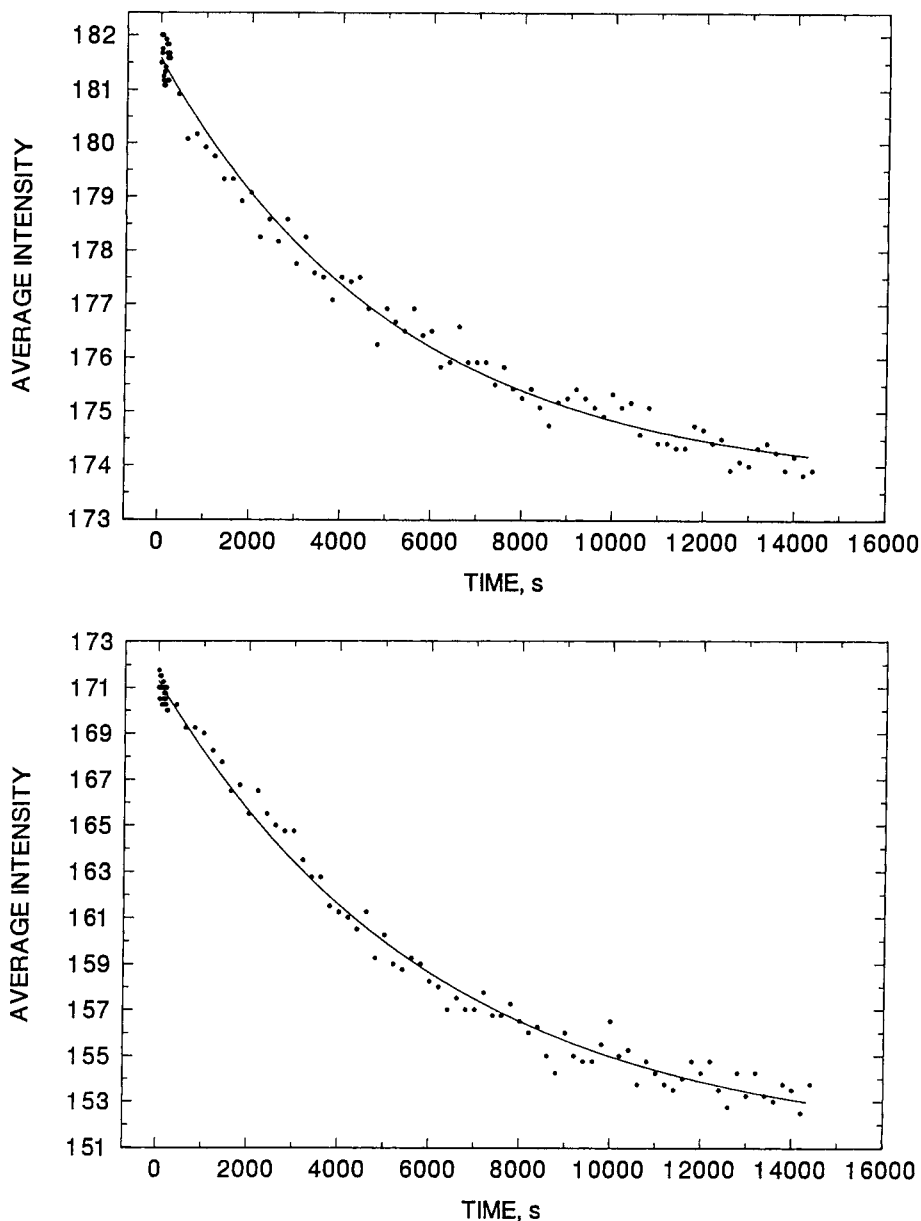
Figure 1   (*Continued from the previous page*)

aware of any work investigating the effects of ultraviolet radiation on the fluorescent species in nylon 66.

The present work examines, using image processing, the effect that exposure to ultraviolet light with a maximum at 366 nm has on both the fluorescence and phosphorescence properties of the gel in nylon 66. We also investigate the possibility that the different types of gel are affected differently by exposure to ultraviolet light.

EXPERIMENTAL

Equipment

The equipment used in this research has been previously described[1] and consisted of a 3-CCD color video camera that provided an RGB signal to a color image processing board in a personal computer. The board was able to convert the RGB information to HSI (hue, saturation, and intensity) values as the data was being acquired. In this research, intensity

was used to characterize the fluorescence and phosphorescence emissions from the gel. The intensity value measured by the image processing system is the average of the red, green, and blue values and is equivalent to the gray level obtained when a black-and-white image is digitized. Thus, a black-and-white camera and digitizing board would have served equally well for the measurements described here. The images were viewed on a monitor connected to the image processing board. The samples were placed on a copy stand between two commercial ultraviolet lamps. Experiments were performed at 69°F in air at atmospheric pressure.

Samples

The nylon 66 gel samples analyzed were from pack screens collected during production runs.

Fluorescence

The ultraviolet lights were allowed to equilibrate for at least 1 h and a pack screen with gel particles on its surface was then placed under the camera and the lamps. The first image was acquired 5 s after initial exposure to the ultraviolet light. Images were then acquired at 10-s intervals up to 205 s. Images were acquired every 200 s thereafter until a total of 92 images were acquired. The gel particles on several pack screens were analyzed using this procedure. Regions in the pack screens containing polymer, but no gel particles, were also examined to determine the extent of a background effect, if present. Gel particles trapped in pack screens are encased in polymer, which could affect the intensity of the gel particles as detected by the image processing system.

Another experiment was performed in which, after the above procedure was followed, the pack screen was kept in the dark for 2 h and the procedure repeated, thus acquiring and saving 92 more images. The purpose of this experiment was to determine if the fluorescence intensity would return to its initial value following this "resting period."

The first image saved was retrieved from memory and displayed on the video monitor. Gel particles appeared almost round in the images, and a rectangular area inside each gel particle was chosen for analysis. The area to be analyzed was chosen by the user by moving a cursor across the image and marking the upper left corner and the lower right corner of the desired area. Software in the C programming language calculated the total intensity of the gel particles and the average intensity per pixel. The same area was analyzed in each of the other images

and total and average intensity values were calculated.

As gel particles were exposed to ultraviolet light, there appeared to be an exponential decay in fluorescence intensity over time, which was representative of a first order rate equation for decay. The fluorescence intensity over time was modeled using the following equation:

$$\frac{I(t) - I_\infty}{I_0 - I_\infty} = e^{-k_1 t},$$

where $I(t)$ is the intensity at any time, t; I_∞ is the intensity as time approaches infinity; I_0 is the initial intensity (at $t = 0$); and k_1 is the rate constant for decay.

Figure 1 shows several plots of the average intensity vs. the length of exposure to ultraviolet light for gel particles from different pack screens and the regression curve fitted to the data points. The regression parameters were determined using SAS statistical software. The regression parameters I_0, I_∞, and k_1 and their 95% confidence intervals for the gel that appears green and the gel that appears red as seen by the naked eye and by the image processing system are shown in Tables I and II, respectively. The polymer on the pack screens was also examined to determine if it behaved differently from the gel when exposed to ultraviolet light, and the results from several analyses are shown in Figure 2. The regression parameters for the nylon 66 polymer samples and their 95% confidence intervals are shown in Table III. No significant difference could be detected using a Tukey test at an α of 0.05 between the means of the decay constants for the red gel particles, the green gel particles, and the polymer. Figure 3 demonstrates the overlap in the 95% confidence intervals of the estimates of k_1.

In one of the experiments, the pack screen was kept in the dark for a period of 2 h between two sets of measurements (at picture number 91). The fluorescence intensity from one gel particle under these conditions is plotted in Figure 4. This plot shows that after exposure to ultraviolet light, the gel particle no longer fluoresces as intensely as it did when first exposed to ultraviolet light. In other words, the fluorescence intensity of the gel recovers only slightly after lengthy exposure to ultraviolet light.

Phosphorescence

A pack screen with gel particles on its surface was placed under the camera and exposed to ultraviolet

Table I   Decay Constants for the Decrease in Fluorescence Intensity with Length of Exposure to Ultraviolet Light for Several Particles of "Green" Gel

Sample	k_1, h^{-1} (95% Confidence Interval)	I_0	I_∞
G1	0.65 (0.61, 0.69)	166.8	160.2
G2	0.50 (0.46, 0.54)	141.8	126.0
G3	0.67 (0.62, 0.72)	143.2	133.5
G4	0.69 (0.35, 1.0)	136.4	135.1
G5	1.0 (0.85, 1.2)	99.0	90.9
G6	0.87 (0.57, 1.2)	118.8	113.5
G7	0.54 (−0.32, 1.4)	142.6	142.1
G8	0.68 (0.42, 0.93)	111.4	106.3
G9	0.69 (0.63, 0.75)	173.7	165.8
G10	0.71 (0.62, 0.79)	187.7	180.6

light for 200 s. The ultraviolet lamps were then turned off and the process of acquiring an image was started 0.010 s later. The image processing system requires 0.033 s to acquire an image to the memory on the board; therefore, the image was acquired within 0.043 s after the lamps were turned off. The image was then saved to the hard drive of the computer. The pack screen was again exposed to ultraviolet light for 200 s and the above procedure was repeated until 90 images were acquired. At this point, the pack screen was kept in the dark for 1.5 h. After this resting period, the above procedure was repeated, and 90 more images were acquired and saved. A second experiment was performed using the method described above, except that the resting period was extended to 36 h. The purpose of having periods of darkness between the acquisition of the two sets of images was to determine if the phosphorescence intensity would return to its initial value following a period of rest from exposure to ultraviolet light. Also, the 36-h period of darkness allowed us to examine any decay in phosphorescence intensity that could occur due to aging over time even in the absence of ultraviolet light.

After the images were acquired and saved, the first image was retrieved from the hard drive and displayed on the video monitor. Gel particles that phosphoresced appeared brighter than the background and were detected by "thresholding" the intensity values. In the first image, the intensity values of the pixels that were detected as gel were used to calculate the total and average intensities. The same area was examined in each of the other images and again total and average intensities were calculated.

The plots of average intensity vs. image number

for phosphorescence intensity with resting periods of 1.5 h and 36 h are shown in Figure 5. There is a large amount of noise in the data. A decreasing trend in phosphorescence intensity as image number increases is evident in both figures. Also, after the resting periods of 1.5 h and 36 h, gel particles could no longer phosphoresce as intensely as they did in the first few images acquired. The phosphorescence intensity was, within experimental error, the same before and after the resting period, indicating that neither recovery nor decay due to aging occurred during the resting period. This leads to the conclusion that the decay in the phosphorescence intensity of the gel particles detected by the image processing system over these periods of time is due mostly to the exposure to ultraviolet light. The noise in the data did not allow the determination of accurate decay constants nor the development of representative equations for the decrease in phosphorescence intensity, but in Figure 5 possible regression curves are illustrated.

SOURCES OF ERROR

The instability of the output from the ultraviolet lamps caused error in the measurements of fluorescence intensity. Even after the ultraviolet lamps approached equilibrium, they emitted light at intensities that oscillated and affected the image by about ± 1 intensity unit. The wave-like fluctuation is apparent in the data and affects the measured decay constants.

There are several other factors that could affect the measured decay constant, k_1, including the distance of the ultraviolet lamps from the sample, the

Table II   Decay Constants for the Decrease in Fluorescence Intensity with Length of Exposure to Ultraviolet Light for Several Particles of "Red" Gel

Sample	k_1, h^{-1} (95% Confidence Interval)	I_0	I_∞
R1	0.95 (0.79, 1.1)	93.6	88.1
R2	1.0 (0.77, 1.2)	90.8	84.8
R3	0.91 (0.70, 1.1)	143.8	138.4
R4	1.1 (0.84, 1.3)	76.0	67.9
R5	1.1 (0.74, 1.5)	118.3	114.3
R6	0.88 (0.77, 0.99)	165.3	156.6
R7	0.59 (0.54, 0.64)	151.0	130.7
R8	0.78 (0.63, 0.93)	137.4	129.2
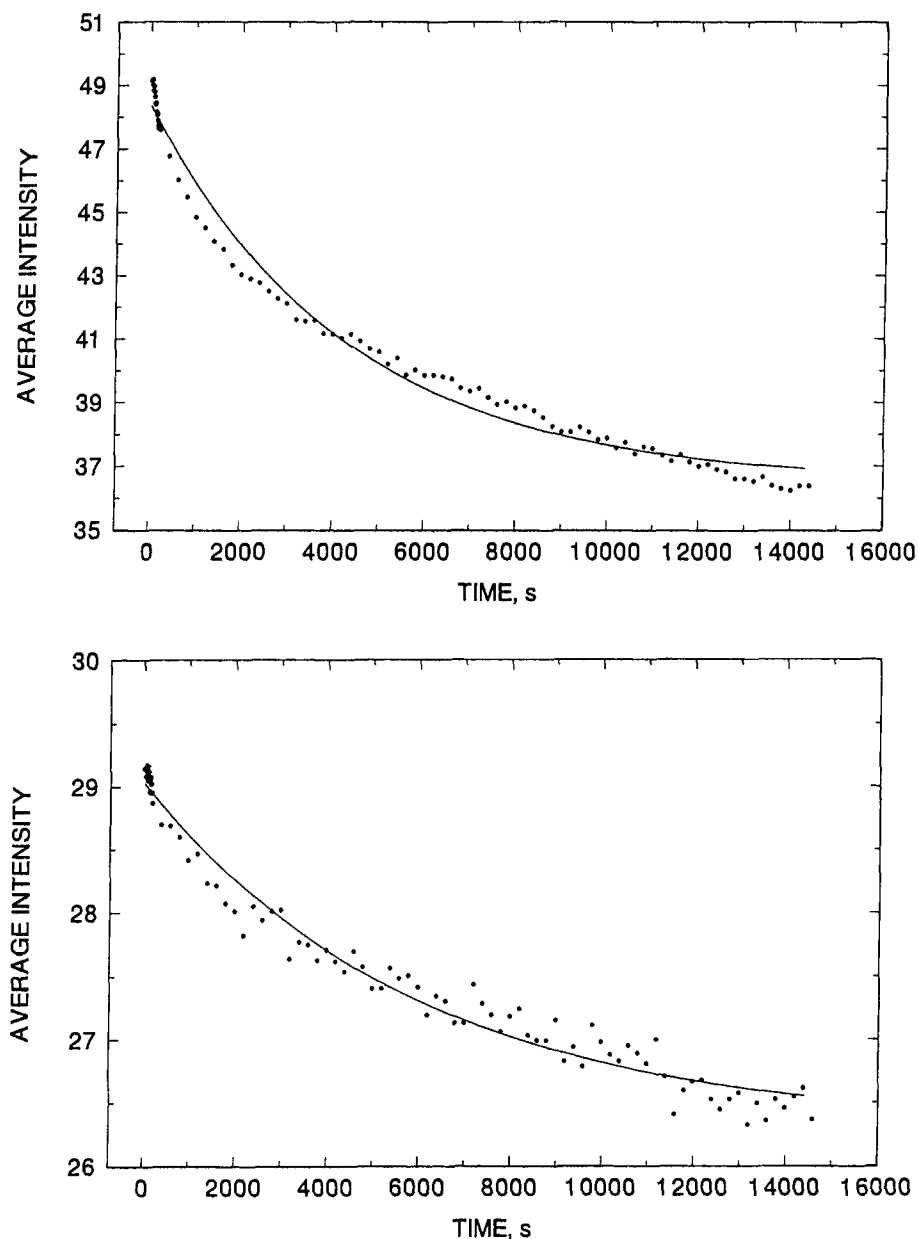
Figure 2 Decrease in fluorescence intensity with length of exposure to ultraviolet light for several regions of the polymer without gel particles.

temperature of the surroundings during experimentation, and the location of the gel particles on the pack screen. The ultraviolet lamps were moved 53 cm apart from their original distance of 37 cm and images of a pack screen were acquired over a 4-h period. Examining the k_1 values of the gel particles analyzed, no significant change in the values of the decay constants was detected as a result of changing the distance between the lamps. Images of pack

screens were acquired over a 4-h period of exposure to ultraviolet light at 59°F and at 79°F. Previous experiments had been performed at 69°F. Decay constants were regressed for both polymer and gel particles. Exposing gel to ultraviolet light in a warm environment affected the measured decay constant. One gel particle examined at 79°F had a regressed decay constant of 2.32 h^{-1} (95% confidence interval: 1.73 to 2.90 h^{-1}), which is greater than decay con-
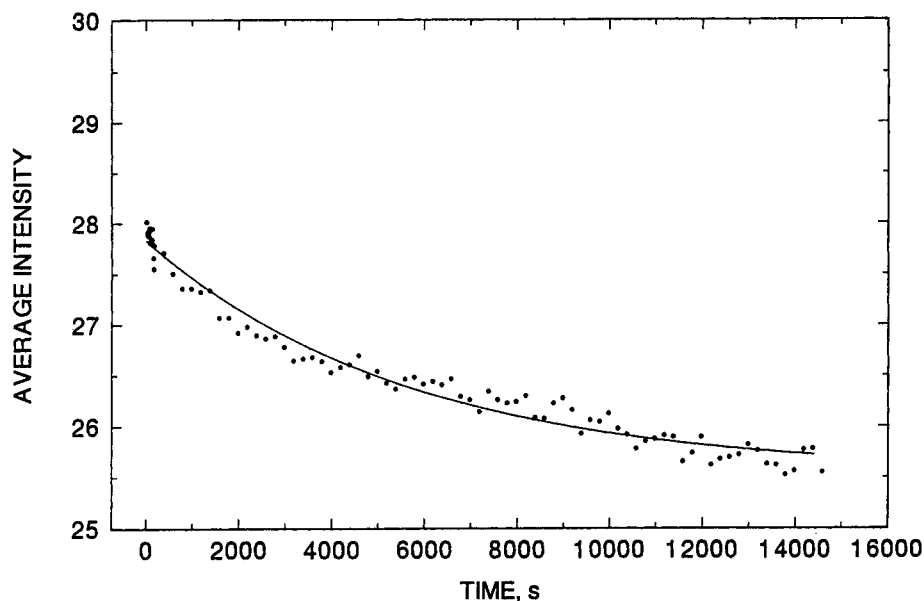
Figure 2   *(Continued from the previous page)*

stants determined in experiments at 69°F. Another gel particle examined at that temperature, though, had a decay constant of 0.58 h^{-1} (95% confidence interval: 0.47 to 0.68 h^{-1}), which is in the range of the decay constants at 69°F. Exposing gel particles to ultraviolet light in a cold environment also affected the decay constants. The fluorescence emissions from two gel particles at 59°F only decreased in value by one intensity unit, indicating that the cold temperature was a hindrance to the decay in fluorescence intensity. One of these gel particles, though, had a decay constant of 0.898 h^{-1} (95% confidence interval: 0.801 to 0.995 h^{-1}), which is

similar to the decay constants at 69°F. The effect of temperature on the decay of fluorescence emmisions when exposed to ultraviolet radiation could possibly be used to distinguish different types of gel. To improve the reproducibility of the results, future experiments should be performed at a constant temperature. The effect of the position of the gel particles on the pack screens in relation to the incident light was also examined. This effect was examined theoretically because of the difficulty in obtaining accurate results experimentally. Figure 6 represents the setup of the lights on the copy stand. Intensity varies inversely with the square of the distance. Thus, if each of the two lamps is considered a line source of light, the intensity, I, of the light reaching any point between them would be the sum of the intensities of the light reaching that point from each of the two lamps:

$$I = C\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right),$$

where C is a constant, and r_1 and r_2 are, respectively, the distances from each of the lamps to that point. Expressing r_1 and r_2 in terms of h, x, and L (refer to Fig. 6), we obtain the following dimensionless equation for the ratio of I_x, the intensity at any point x on the copy stand, to I_c, the intensity at the point on the copy stand midway between the two lamps $(x = 0)$:

Table III   Decay Constants for the Decrease in Fluorescence Intensity with Length of Exposure to Ultraviolet Light for Several Regions of the Polymer

| Sample	k_1, h^{-1} (95% Confidence Interval)	I_0	I_∞
P1	0.69 (0.64, 0.74)	97.6	84.5
P2	0.27 (0.14, 0.39)	29.1	27.6
P3	0.60 (0.52, 0.68)	26.3	23.6
P4	0.64 (0.55, 0.72)	25.5	23.2
P5	0.85 (0.77, 0.94)	31.0	22.7
P6	0.84 (0.76, 0.91)	36.5	24.6
P7	0.98 (0.87, 1.1)	69.7	61.8
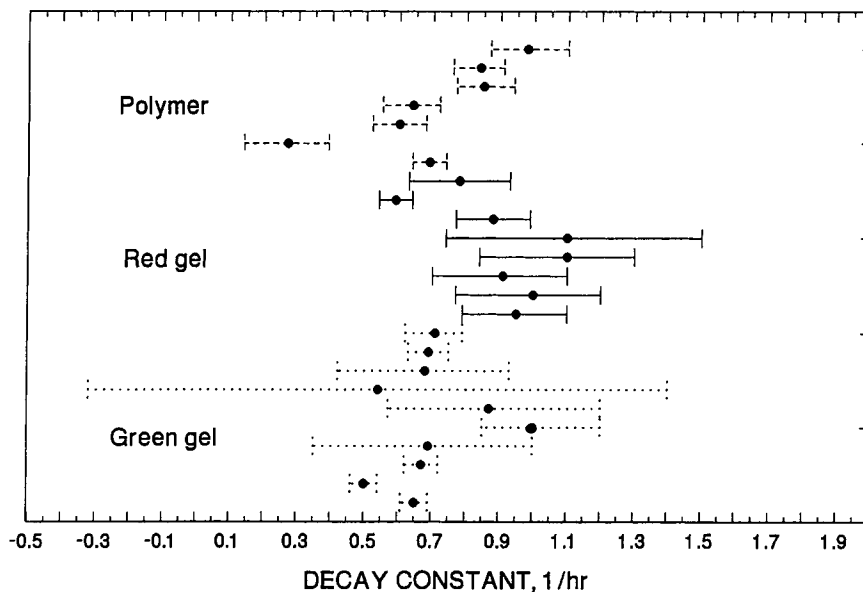
Figure 3 Decay constants and their 95% confidence intervals for green and red gel particles and for the polymer.

$$\frac{I_x}{I_c}$$

$$= \frac{\dfrac{1}{(h/L)^2 + (1 - x/L)^2} + \dfrac{1}{(h/L)^2 + (1 + x/L)^2}}{\dfrac{2}{(h/L)^2 + 1}} .$$

For our system, h is 12 cm and L is 18.5 cm. The radius of a pack screen is 4 cm so that x/L is 0.22 at the edge of a pack screen. A plot of I_x/I_c vs. x/L (Fig. 7) shows only about a 6% change in I_x/I_c at $x/L = 0.22$ (the edge of the pack screen) as compared to its value at the center where $x/L = 0$. Therefore, a gel particle on the edge of a screen and a gel particle in the center of a screen will receive approximately
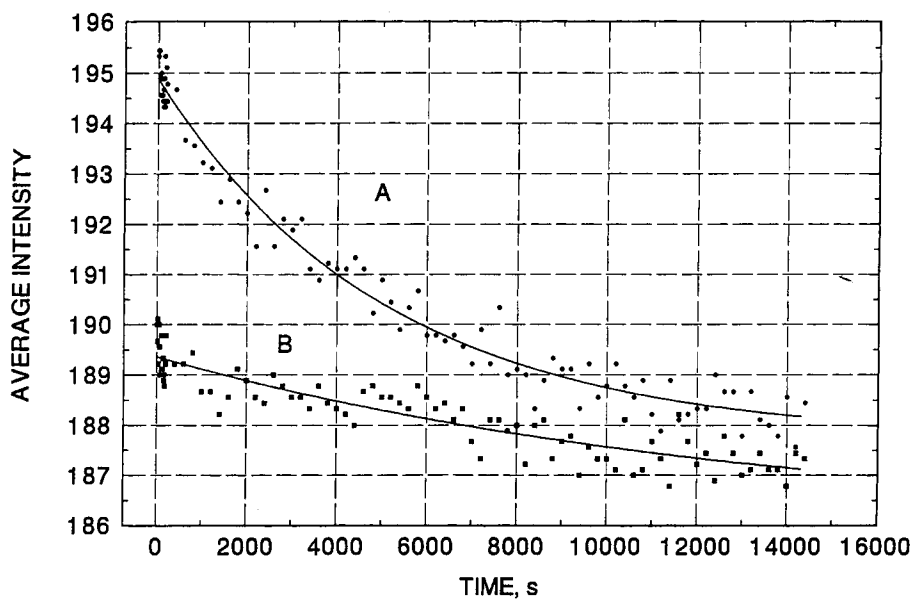
Figure 4 Decrease in fluorescence intensity of a gel particle with length of exposure to ultraviolet light (curve A) and a second set of measurements after two hours without exposure (curve B).
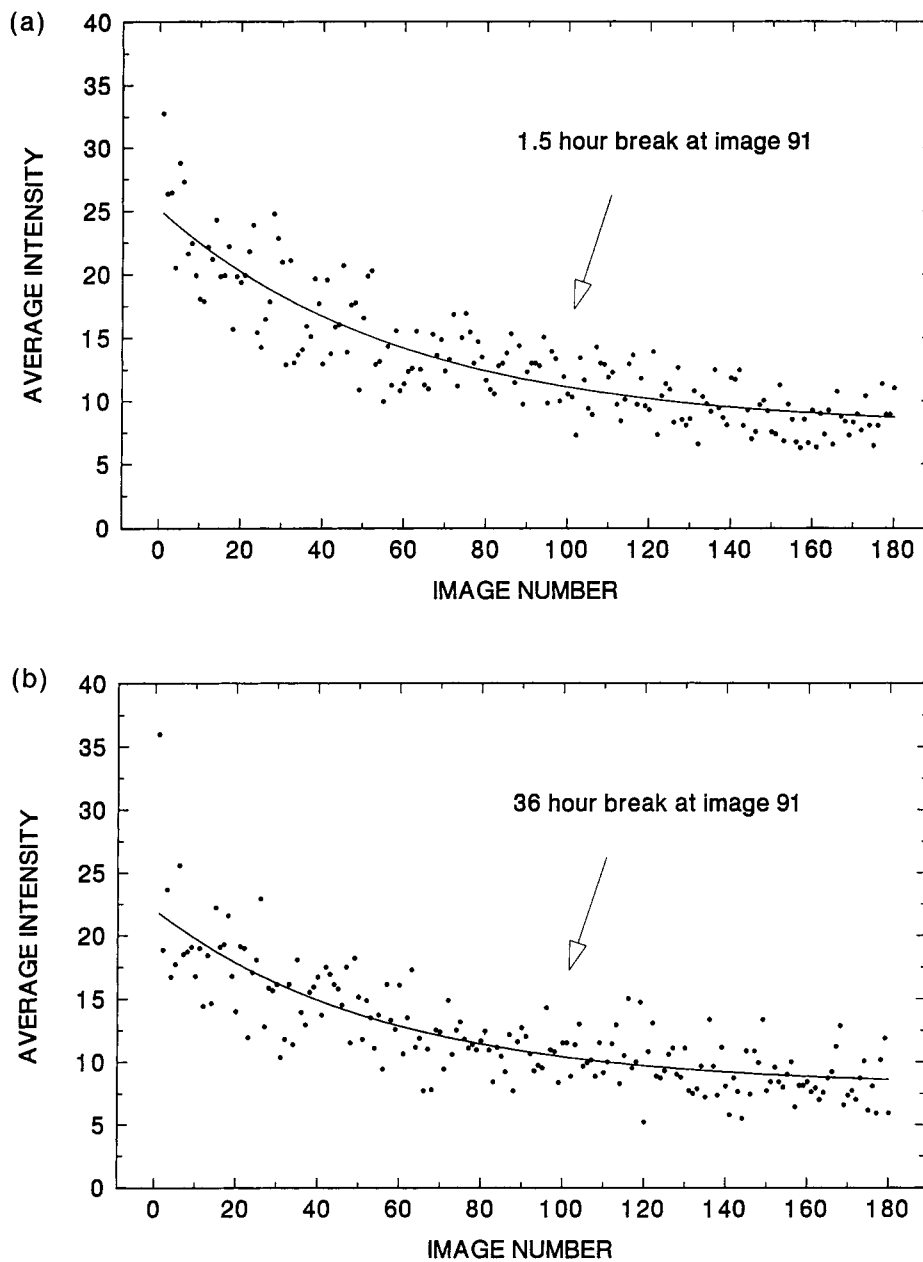
Figure 5 Decrease in phosphorescence intensity with exposure to ultraviolet light. At image 91, no images were acquired for (a) 1.5 h or (b) 36 h, and the gel was not exposed to ultraviolet light during this period.

the same incident intensity of light from the ultra-violet lamps.

Noise is evident in the phosphorescence measurements. The low intensity of the phosphorescence emissions required the camera to be used on its highest gain, which resulted in loss of image resolution and in error in the intensity values measured using the image processing system.

Another source of error is the nonlinear relationship between the intensity of the light impinging on the camera and the intensity value measured by the image processing system. Intensity as measured by the image processing system was calibrated using a light meter and the results are shown in Figure 8. Because the range of intensity values in our experiments was small, linearity was assumed.
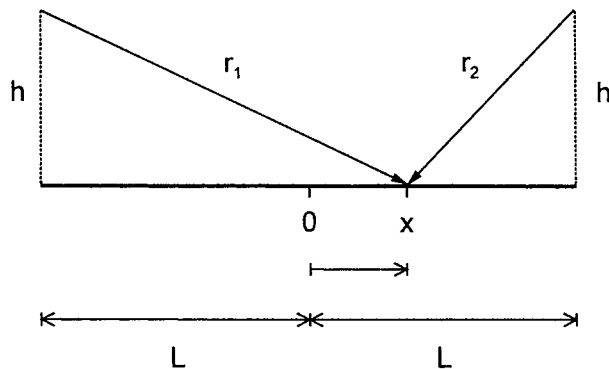
Figure 6 Diagram representing the distance from the ultraviolet lamps to different locations on the sample.

CONCLUSIONS AND RECOMMENDATIONS

The fluorescence emissions from the green and the red gel particles decreased in intensity exponentially with the duration of the exposure to ultraviolet light. The fluorescence from the polymer on the pack screens, although much lower in intensity than that from the gel particles, was affected by the ultraviolet light in a similar fashion. The decay constants for the two types of gel particles and for the polymer were found to be in the same range within experimental error. It, thus, may be possible that a similar mechanism is responsible for the decrease in the

intensity of the fluorescence emissions from both the gel and the nylon 66 polymer. Previous research has indicated the presence of impurities in nylon 66 that have luminescent properties in the ultraviolet region, and changes in these gel species may be responsible for the change in the fluorescence intensity of the polymer. Gel cannot completely regain its original fluorescence intensity after exposure to ultraviolet light, even after a rest from exposure, which indicates that a permanent change in the structure of the gel has occurred.

The phosphorescence intensity of the gel particles also decreased with continued exposure to ultraviolet light. The phosphorescence intensity did not return to its original value after a long exposure to ultraviolet light, indicating that the structure of the gel had been permanently altered. Accurate decay constants could not be regressed from the phosphorescence data because of the noise in the data. To obtain data with less noise, we recommend that a camera with greater sensitivity, even if it is a black-and-white camera, be used in future analyses of the phosphoresce properties of the gel particles.

The relationship between the decay of fluorescence and phosphorescence emissions and the structure of the gel should be further investigated. The effect of temperature on the decay of the fluorescence properties should be examined because it may be possible to distinguish the polymer degradation from the gel degradation and to distinguish
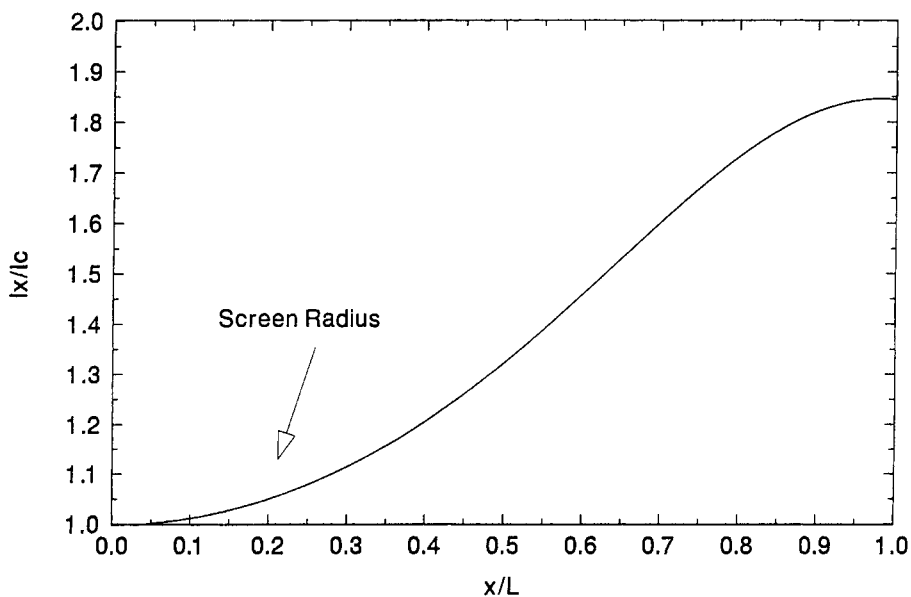
Figure 7 Theoretical change in the incident light intensity as a function of distance from the center of the copy stand.
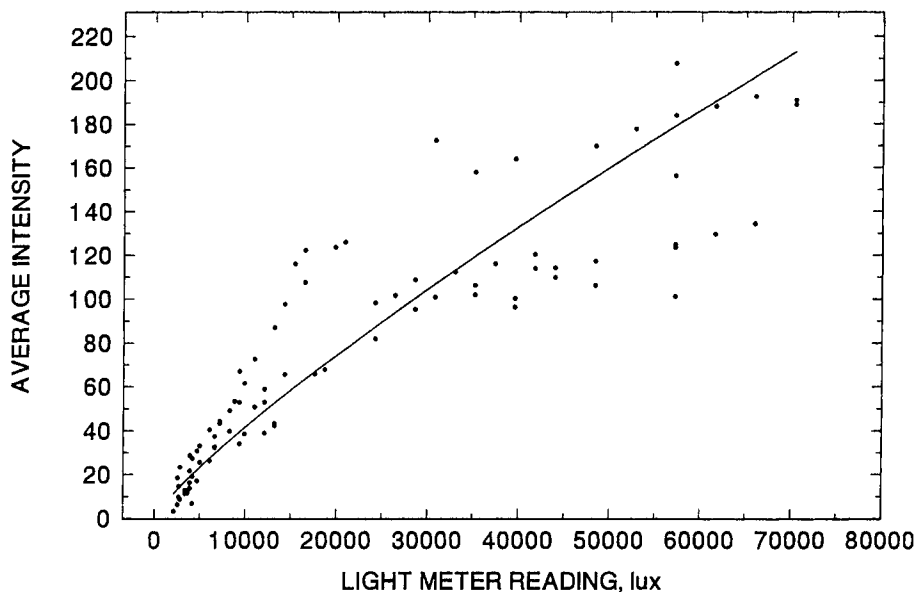
Figure 8 Correlation between the average intensity detected using the image processing board and light intensity measured by a light meter.

between different structures of gel. Analyzing the fluorescence intensity decrease when gel particles are exposed to ultraviolet light at different temperatures may lead to finding the activation energy for the decrease in intensity due to exposure to ultraviolet light.

This research may be relevant to other applications where fluorescence and/or phosphorescence properties of a substance are examined, because the properties and structure of the substance may be altered by the radiation source. Image processing provides a simple and inexpensive method for luminescence analysis of gel compared to other spectroscopic techniques. A camera that detects emission in the ultraviolet region or infrared region could possibly be used to examine fluorescent and phosphorescent emissions from nylon 66 outside the visible region.

REFERENCES

1. C. R. Brasington and F. Gadala-Maria, *J. Appl. Polym. Sci.*, **53**, 747 (1994).
2. H. A. Taylor, W. C. Tincher, and W. F. Hamner, *J. Appl. Polym. Sci.*, **14**, 141 (1970).
3. N. S. Allen, J. F. McKellar, and G. O. Phillips, *J. Polym. Sci., Polym. Chem.*, **12**, 1233 (1974).
4. N. S. Allen, J. F. McKellar, and G. O. Phillips, *J. Polym. Sci., Polym. Chem.*, **12**, 2623 (1974).
5. N. S. Allen and M. J. Harrison, *Eur. Polym. J.*, **21**, 517 (1985).
6. H. H. Dearman, F. T. Lang, and W. C. Neely, *J. Polym. Sci. A-2*, **7**, 497 (1969).
7. J. A. Dellinger, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 167 (1976).
8. L. H. Peebles, Jr., *J. Polym. Sci. A-1*, **9**, 1807 (1971).
9. L. F. Hatch and S. Matar, *From Hydrocarbons to Petrochemicals*, Gulf Publishing, Houston, 1981.