DELAYED DARKENING OF RADIATION-EXPOSED RADIOCHROMIC Dye DOSIMETERS

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Abstract

Thin dosimetry films, type FWT-60, consisting of hexahydroxyethyl paraarosanline cyanide in a Dupont Nylon resin, have been found to exhibit a considerable delayed darkening that may, depending on relative humidity, last for tens of hours at room temperature, until full color saturation is reached. Erroneous dosimetry measurements may therefore result if optical density measurements are made before this delayed darkening has proceeded to saturation. This effect has been investigated using both 1 MeV electrons and Co-60 gamma rays, and has been found to be independent of dose rate in the range 0.7 to 70 Gy, radiation species (electrons or gamma rays), and the percentage of total radiation dose which it represents. The amount of delayed darkening, i.e., the percentage of optical density at saturation, was found to depend very strongly on the relative humidity at which the films were equilibrated a few hours before irradiation. The delayed darkening which remained 10 minutes after irradiation was found to be 45% for nominal 0% RH (1 hour in vacuum), 23% for 25-35% RH, and less than 3% for 65-75% RH. Heating the films for 1 minute at 45°C effects a decrease in delayed darkening from 45% to 20%, and for 5 minutes, the decrease is to less than 5%. A number of recommendations are made to account for delayed darkening in FWT-60 films in order to maximize accuracy and repeatability of dosimetry measurements.

Introduction

A Far West Technology (FWT) radiochromic dye dosimetry system was acquired for use by the Radiation Facility of Goddard Space Flight Center to complement and act as a check on the existing dosimetry systems.

A number of dosimetry films were sent to the NBS, where they were irradiated with calibrated sources of gamma rays to specified total accumulated doses. When the optical density (OD) of these films were read on the FWT radiochromic reader, the results were correct to within ±10% for doses in the range 10^3-10^6 Gy. However, when the system was used with fresh films from the same batches to measure absorbed doses of gamma rays and electrons, inconsistencies were observed in the read-outs. It was when it was observed that the dosimetry films calibrated by the NBS produced consistently correct dose response, and attention was directed to films freshly exposed to radiation, that this delayed darkening effect was discovered.

The purpose of this paper is to investigate the delayed darkening effect in terms of total dose and dose rates of both gamma rays and electrons, laboratory conditions, such as humidity and temperature, and from the user's point of view, to recommend to the radiation effects community the kind of precautions which should be taken in regard to delayed darkening and what preliminary measurements must be made, if meaningful and accurate dosimetry is to be attained.

This paper deals with the effects of relative humidity, dose rate and total dose on the delayed darkening. Gehring et al. investigated the effects of the above parameters on the total sensitivity of the films at saturation and found that there is a dose rate and total dose dependence of the sensitivity and also a dependence on the relative humidity at which the films were equilibrated before irradiation.

Radiochromic Dosimeters

Chalkley was the first to report that solid solutions of various aminotriphenyl methane dye derivatives with certain organic activators were sensitive to ionizing radiation. McLaughlin and Chalkley have demonstrated that stable coloration of the dye cyanides in plastic films exposed to electron beams can be obtained and suggested that they may have a potential usefulness as high-dose dosimetric materials. Humphreys and Wilcox and Humphreys and Kantz demonstrated the use of nylon as a solid activator solvent in the form of unsupported thin films. Further studies on the properties of these dosimetry films were done by McLaughlin and his co-workers.

There are various aminotriphenyl dye derivatives, but the particular radiation-sensitive compound used in the FWT-60 films is the hexahydroxyethyl paraarosanline cyanide within the Dupont Nylon resin, Elvanite 8061, which forms the host matrix of a solid state solution. The radiation-induced photochemical reaction involved there is a unimolecular decomposition of the dye derivative, followed by an intramolecular electron rearrangement to form the stable and deeply blue colored dye. The degree of coloration is a measure of that dose, which may be read with a spectrophotometer or a simple photometer. Recent measurements by McLaughlin et al. and by Gehring et al. indicate that there is a dose rate and total dose dependence of the sensitivity and also a dependence on the relative humidity at which the films are equilibrated before irradiation.

Delayed Darkening

Nablo and Tripp reported a considerable delayed darkening effect, or long-term color development. They observed that in FWT-60 film, read about 40 seconds after irradiation, only about 50% of total color saturation had occurred. After that, it took more than 10 hours to reach a complete color saturation and stability. Unfortunately, no data on the relative humidity before, during or after irradiation were given. Chappas demonstrated that the rate of color development and the time required to reach full color saturation depends strongly on the relative humidity at which the film samples were equilibrated before exposure to radiation. It was also shown that heating of the samples after irradiation for just one minute at 45°C decreased the time required for full color saturation to about one half.

Experimental

FWT Model 401 Radiochromic Dosimetry System

The instrument consists of a photometer containing a standard tungsten lamp, two narrow optical band pass filters, one at 600 nm for high sensitivity (<20 k Gy) and the other at 510 nm for low sensitivity (10 k Gy - 200 k Gy) and a sensitive P-on-N silicon solar cell. The reader is provided with two calibration curves, one for each wavelength. The reader is designed to be used with FWT radiochromic dosimeters with a film holder for 1 x 1 cm cut film. The film pieces are placed in the holder which has a 3 mm hole for light transmission. The light transmitted through the dosimeter is received by the silicon solar cell, fed into an operational amplifier, and the signal output is displayed on a meter. Read-out on the meter is either in percent transmission or optical density. The change in optical density is directly proportional to the absorbed dose and may be read from the calibration curves, taking into account the relative sensitivity of the film. In practice, the reader has proven to be quite reliable, stable and easy to use.

*Trade names used in this paper do not imply endorsement for any particular product, but are merely used for proper identification.
The radiochromic film used in these experiments was manufactured by, and commercially available under the code FWT 60 and 65, from Far West Technology, Inc. It was acquired in both precut (FWT-60) and sheet (FWT-65) form. In precut form it was supplied in pieces of about 1 cm × 1 cm × 2 mil, preselected by the manufacturer according to thickness and grouped in lots according to sensitivity.

Experimental Procedure

The films were irradiated with both CO-60 gamma rays in an AECL Gamma-cell and 1 MeV electrons from the 2 MeV Van de Graaff accelerator. Irradiations were carried out with and without aluminum shields of various thickness, in order to obtain electron equilibrium in that material. Readings were conducted immediately after irradiation with the system described above. Once the settings of the reader were made, they were not disturbed during a complete experiment, as we found the drift of the system was less than if corrections were made before and after each measurement. The time of the delayed darkening process was measured from the middle of the irradiation period. Because the films are sensitive to UV light, they were protected from sunlight and from fluorescent illumination during storage and handling. Exposure to fluorescent illumination for short periods of time during the read-out was found not to introduce any measurable effect on the films. Film samples were irradiated in groups of five and the results given in this paper are averages of five read-outs, unless stated otherwise.

To increase the accuracy of the measurements for this paper, the meter was disconnected from the instrument and the output of the operational amplifier was fed into a Keithley Model 445 picoammeter. The optical density is then found using the relation:

\[
OD = \log_{10} \left( \frac{1000}{I} \right)
\]

where \( I \) is read directly from the picoammeter in tenths of \( \mu A \). The Keithley model 445 Picoammeter reads to three significant figures, and three significant figures are carried throughout the dose calculations. The rounding-off necessitated by this procedure results in a maximum sensitivity of the total system of approximately \( 7 \times 10^{10} e/cm^2 \), or 25 Gy. When the data are presented in terms of a percentage of saturated value, this results in a maximum error, in the case of a total dose of \( 9 \times 10^{11} e/cm^2 \), of ±5%.

Before irradiation, the films were preconditioned at the temperature and relative humidity which existed at the time of the experiments in our laboratory. In some experiments, however, in order to observe the effect of preconditioning at 0% RH, the samples were placed in vacuum for one hour before irradiation and irradiated in vacuum. The films were then always read at the existing temperature and relative humidity in the laboratory. Altogether there were three environmental conditions for preconditioning and read-out of the samples:

<table>
<thead>
<tr>
<th>Preconditioning RH:</th>
<th>Read-out RH:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  25-35%</td>
<td>25-35%</td>
</tr>
<tr>
<td>2  65-75%</td>
<td>65-75%</td>
</tr>
<tr>
<td>3  0% (1 hour vacuum)</td>
<td>65-75%</td>
</tr>
</tbody>
</table>

Both temperature and humidity were recorded continuously by a Honeywell model 612X9-H-111-111-7E162 Temperature and Humidity Recorder.

Results and Discussion

Results are presented in the form of graphs, where the amount of delayed darkening, i.e., apparent dose, is presented in units of electron fluence, gamma ray dose or percentage of total color saturation as a function of color development time. In the case of electron fluence (Figs. 1, 2 and 4), a conversion factor of \( 1 \times 10^{12} e/cm^2 \) (1 MeV) = 350 Gy was used in order to make use of the calibration curves supplied with the Reader. In the case of gamma rays (Fig. 3), the doses were read directly from the calibration curves. The reason for presenting the data in this way is to enable the reader to see the total doses to which the films were exposed, the type of radiation and the apparent doses or fluences the delayed darkening represents. In Figures 5-7, the amount of delayed darkening is given as the percentage of total color saturation, and is defined as:
Figure 4. Comparison of delayed darkening after high and low total radiation dose.

Figure 5. Normalized delayed darkening of the three total doses of Figures 1 and 4.

Figure 6. Effect of relative humidity on delayed darkening.

Figure 7. Effect of heating at 45°C immediately following irradiation. Relative humidity: 1 hour at vacuum before and during irradiation, at read-out 65-75%.

\[
\frac{D \text{ (immediately after irradiation)}}{D \text{ (saturation value)}} \times 100\% \text{ of saturation,}
\]

where D is the radiation dose obtained from the calibration curve supplied with the films. (In the region of interest here, the indicated dose, D, is a linear function of the change in optical density, \(\Delta OD\), of the films, i.e., OD (after irradiation) – OD (before irradiation).

Time Dependence of Color Development

A typical example of the delayed darkening effects is shown in Figure 1, where the indicated radiation dose in one individual film sample is plotted vs. logarithm of time, after exposure to a total fluence of \(4 \times 10^{12}\) particles/cm\(^2\) (1 MeV electrons) as measured by a Faraday Cup. As can be seen, the delayed darkening shows almost a straight line increase on a log (t) scale to saturation, with a slight “hump” at the point of saturation. This hump is apparent in almost all of the curves and has been reported in Reference 14.

Dose Rate and Shielding Independence

The delayed darkening effect was investigated for dose rate independence by irradiating different sets of samples with electrons at the following dose rates: \(2.0 \times 10^9\), \(3.5 \times 10^{10}\) and \(2.0 \times 10^{11}\) e/cm\(^2\)/sec., up to the same total dose of \(4.5 \times 10^{12}\) e/cm\(^2\) in each case. As can be seen in Figure 2, the curves are very similar in both slope and final saturation value, indicating that there is no dependence of the delayed darkening on dose rate in this dose rate range.

The amount of delayed darkening seems to be also independent of the presence or absence of aluminum shields and their thicknesses, except for obvious attenuation in electron experiments. Figure 3 shows the delayed darkening for “nude” films (free-standing in air) and 0.038 inches and 0.250 inches of aluminum on both sides of the films. In this case irradiations were performed with CO-60 gamma rays. The scatter of the data points in the data of these two previous figures is larger because the data were taken before the output of the reader was connected to the Keithley microammeter.

Total Dose Dependence of Delayed Darkening

One of the most important results of these measurements is that the time required for completion of delayed darkening, or color development, depends on the total dose imparted to the dosimetry films. This is demonstrated in Figure 4 for two total doses of \(9 \times 10^{11}\) e/cm\(^2\).
and $9 \times 10^{12}$ e/cm$^2$. Whereas saturation value is reached in about one hour for the total dose of 315 Gy, it takes about nine hours to reach saturation for the total dose of 3150 Gy.

If the data for Figures 1 and 4 are normalized, as is done in Figure 5, it is seen that the percentage of delayed darkening is the same for all three total doses, namely, about 23% for the time for 10 minutes after irradiation until saturation. The time to reach saturation, however, is clearly greater for larger doses. When the data of this figure is examined more closely, however, we observe that, although the saturation point is reached sooner for smaller doses, the stability of the read-outs is reached much later because of larger humps for these small doses at or near saturation levels. Thus, if one is looking for both saturation and stability of the read-outs, then one must wait at least nine hours at this relative humidity range. Our findings agree with those of Reference 14, although no relative humidity was identified there.

Relative Humidity Effect

The effect of relative humidity for both preconditioning time periods and time periods immediately following irradiations is shown in Figure 6 for the total dose of $9 \times 10^{12}$ e/cm$^2$. Curve A is for 25-35% RH for both the preconditioning period and the read-out period. Curve B is the same as A except for 65-75% RH. Curve C has one hour of vacuum preconditioning followed by read-out at 65-75% RH. When placed in vacuum for one hour, it is expected that the samples would lose most of their water content through desorption, as experimentally determined by Chappas.13 Indeed, the samples exhibit a much larger delayed darkening, starting on the average with only 55% of color development 10 minutes after irradiation as compared to about 77% in Figure 5. Although the samples initially exhibit a straight line, i.e., logarithmic behavior of color development for a few tens of minutes, the color development deviates from a straight line for longer times because large quantities of water are being absorbed at this high relative humidity, obscuring the total dose dependence somewhat, and saturation levels are reached sooner than in Figure 5. Some evidence of total dose dependence may be also observed here by extending the initial slopes of the curves as shown in the figure. However, one should expect that even these initial slopes were affected by absorption of moisture from the ambient.

As one can see from these data, relative humidity plays a strong role in the amount and mode of delayed darkening. Preconditioning at 65-75% RH makes the delayed darkening disappear almost altogether. On the other hand, pretreatment in vacuum for just one hour before irradiation, which is equivalent to preconditioning at 0% RH, increases the amount of delayed darkening to 40-50% which is still there 10 minutes after irradiation. What can also be concluded from these data is that the time required for complete color development, or saturation, depends strongly on the relative humidity at the read-out as well, since most of the absorption or desorption of the water in these films takes place in a time period of less than one hour.15

Post-Irradiation Heating Effect

Figure 7 shows the effect of heating the films immediately after irradiation at 45°C. (Heating was done on a half inch slab of aluminum located inside a Lab-Heat Muffle Furnace, Blue M Electric Co., Model M15A-1. The furnace together with the aluminum slab was preheated at 45°C for several days in advance.) All the samples were preconditioned in vacuum for one hour. Curve A represents samples with no heating. Samples of curve B were heated for 1 minute at 45°C and the samples for curve C for 5 minutes. As can be seen, the effect of heating is dramatic; heating for only 1 minute reduces the delayed darkening from 45% to 20%, and heating for 5 minutes reduces it to less than 5.

Delayed Darkening

The chemical processes leading to delayed darkening, or causing the slow color development in these thin Nylon dosimetry films, are as yet not well understood and work is being done in this area. Recent work done by McLaughlin et al.16 on the study of kinetics of dye formation by pulse radiolysis of pararosaniline cyanide in aqueous or organic solutions indicated that the radiation-induced conversion of the dye to the highly colored salt-isomer of the dye, takes place in two separate processes. The first is very fast (within <50 ns), and the second much slower, following first-order kinetics with a rate constant that increases as the acidity or concentration of an oxidizing agent increases. One would expect that a similar two-step process of radiation-induced dye formation takes place in the Nylon host matrix. The fact that Nylon is relatively hydrophilic and the presence of water greatly speeds up the radiation-induced dye formation, indicates that what we are dealing with here is a solvent-related diffusion process. This is further substantiated by the work of Gehringer et al.1 where they found that when the films are irradiated after preconditioning at nominal 0% RH, a second absorption band at 412 nm appears, which is converted completely to an additional 606 nm absorption band by exposure to a humid atmosphere. The experiments suggest that initially, during irradiation, the species responsible for the 412 nm absorption are formed. At higher moisture content inside the film, these species are immediately converted to the final dye. Since the purpose of this paper is to characterize the delayed darkening from a dosimetry viewpoint and not to explain its cause, the reader is referred to the works cited above for further discussions.

Conclusions and Recommendations

Experiments have verified the existence of considerable delayed darkening in FWT-60 dosimetry films, that may, depending on relative humidity, last for several hours. The amount of delayed darkening depends very strongly on the relative humidity at which the films are equilibrated before irradiation: 10 minutes after irradiation the delayed darkening for nominal 0% RH (1 hour in vacuum) is about 45%, for 25-35% RH it is about 23%, and for 65-75% RH it is less than 3%. These percentages were found to be the same for total doses of $9 \times 10^{11} - 9 \times 10^{13}$ e/cm$^2$ 1 Mev electrons. The time period required for completion of full color development was found to be total dose dependent. The effect, however, was found to be independent of dose rate in the range of $2 \times 10^9 - 2 \times 10^{11}$ e/cm$^2$/sec, and also independent of the type of radiation, i.e. electrons or gamma rays. The data presented in this paper are not intended to be a detailed study of the effect of each of these parameters on the delayed darkening, but rather an indication of the relative importance of each parameter. From the above experiments, it is clear, however, that the delayed darkening effect must be taken into account before any meaningful dosimetric measurements may be made using these Nylon-based thin dosimetry films. It is up to the individual user to calibrate the delayed darkening under the conditions prevailing in his installation.

As a result of the above experiments, the following recommendations can be made:

1. The delayed darkening effect as a function of total dose must be measured, similar to the data presented in Figure 5.
2. A number of such data sets should be obtained for all the relative humidities encountered at the dosimetry measurement site.
3. The delayed darkening effect can then be accounted for and corrected by noting the time starting from the middle of the radiation time period until the measurement is to be made. For more accurate results, however, it is best to wait until delayed darkening is completed, and the point of saturation is reached.
4. Another option is to heat the dosimetry films at about 40-50°C for several minutes, if a quick read-out is desired. In this case, a set of data similar to that of Figure 7 has to be established.

Other precautions and recommendations concerning the use of the FWT dosimetry system:

1. For more consistent results it is best to obtain the films in sheet form, and later cut them to 1 cm squares, rather than in precut and
In presorted lots the film pieces were found to be of various thickness, but the variations in thicknesses were found not to correlate with variations in sensitivity.

2. If the film holder of the FWT Reader is found to be too loose, it may be tightened by wrapping a layer or two of Scotch tape around it and covering the locating pin with a layer of epoxy or cyanoacrylate adhesive.

3. The outer box containing the meter is made of wood. If for any reason the meter has to be taken out and the retaining screws unscrewed, extreme care must be exercised not to let wood dust get into the optical components or sample holder of the reader. It is best to cover the unvarnished wood with shellac or paint before reassembly.

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References