PRESAGE™ - Development and optimization studies of a 3D radiochromic plastic dosimeter – Part 1

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1. Introduction
Interest in a 3D dosimeter made of transparent plastic can be traced back to the early 1960s [1]. Since that time there have been general formulation approaches attempted but with limited success. The first approach is to dissolve a preformed polymer, such as poly(methyl methacrylate), in dichloromethane along with the radiochromic components. Moskovitch [2] used this approach in making a small cubed neutron dosimeter of only several mm³. The primary limitation to their approach is that as the solvent evaporates a polymer “skin” is formed which effectively prevents the remaining solvent from evaporating even after the addition of heat or vacuum, consequently, limiting the size of the dosimeter. The second approach is heating a low melting transparent polymer such as polyethylene-co-polybutylene and mixing the radiochromic dye into the molten plastic and allowing it to cool³. The basic limitations of this approach are that most leuco dyes will turn color at elevated temperatures. A uniformly mixed dosimeter was difficult to obtain. Consequently, only relatively small dosimeters have been manufactured. In this paper we studied the polymerization of six different transparent plastics as potential 3D dosimeter matrices. In addition, six different leuco dyes and sixteen different free radical initiators were evaluated. Finally, the photoreactivity of the dosimeter was studied so that the effect of exposure to UV could be minimized.

2. Materials and methods
Potential dosimeter formulations were prepared in plastic cuvettes (1 x 1 x 4 cm³). The dosimeters were irradiated using a Varian 600C linear accelerator with a 4 MV photon beam. Three different transparent plastics were evaluated. There were six leuco dyes evaluated and their molecular structures are shown in Fig 1.
In choosing the optimal initiator four factors were considered, stability during manufacturing, overall radiation sensitivity imparted to the dosimeter, and pre and post irradiation dosimeter stability. Free radical initiators that were evaluated at 1-2% were carbonyl based, halocarbons, organoperoxides, and sulfur compounds. The dosimeters formulations were irradiated to doses ranging from 10 cGy to 60 Gy with a dose rate of 250 cGy/min and resulting change in optical density was measured on a Hitachi-Perkin Elmer 204 absorption spectrometer at 630 nm.

The photoreactivity of the optimal formulation was studied so as to minimize the response to artificial lighting and readout with optical CT scanners. Three approaches to reduce photoreactivity were evaluated; addition of UV inhibitors (0.1 – 1%) to the dosimeter, spray outside of the dosimeter with UV inhibitors, filter out the UV emissions from the fluorescent lighting (up to 450 nm). The modified dosimeters were exposed to fluorescent room lighting (approximately 600 lm/m²) and the photochromic background (optical density) was measured over 24 hr.

3. Results

Epoxy and polyurethane polymer based transparent plastic dosimeters were evaluated as potential matrices for 3D dosimeters. The other potential transparent plastics - acrylates, polyesters, polystyrenes and polycarbonates were dropped from further consideration due to the relatively high heat (>100°C) measured during their polymerization, which would degrade the leuco dyes. The epoxy based dosimeters did not consistently respond when irradiated. In contrast, the polyurethane raw materials are mixed and polymerized at room temperature and when irradiated at 10 Gy the polyurethane dosimeters were dose responsive.

Table 1 lists the visible maximums of the six leuco dyes and the relative order of their reactivity. The triphenylmethane leuco dyes, LMG (I) and TLA (II) were the most responsive followed by CVL (III) and the fluorans. LMG has a visible maximum at 633 nm and TLA has an absorbance maximum at 623 nm.

The only group of free radical initiators that are responsive to high energy radiation are the halocarbons. They consistently produce oxidized leuco dyes under a variety of concentrations. The sensitivity of the dosimeters is directly related to the type of halogens contained in the initiator.

![Figure 1. Molecular structure of leuco dyes studies](image-url)
Table 1. Visible maximums of the 6 radiation product dyes studied

| Leuco Dye              | Dye – absorption peak (nm) | Relative Reactivity* |
|------------------------|----------------------------|----------------------|
| Leuco malachite green  | 633                        | 1                    |
| TLA-454                | 623                        | 2                    |
| Crystal violet lactone | 609                        | 3                    |
| Green diaminofluoran   | 575 & 635 (broad)          | 4                    |
| Orange aminofluoran    | 552                        | 4                    |
| Black fluoran          | 570 & 610 (broad)          | 4                    |

*Number 1 is the most reactive and 4 the least

Table 2. Exposure of LMG based dosimeters to fluorescent based room light

| Time (hr)                  | Initial (cm$^{-1}$) | 24 hr (cm$^{-1}$) |
|----------------------------|---------------------|-------------------|
| Room light                 | 0.175               | 1.548             |
| Control – sample kept in the dark | 0.175               | 0.172             |
| UV inhibitors (Benzotriazoles) | 0.192               | 0.953             |
| UV Coating                 | 0.351               | 1.121             |
| Light Source Filter (Amber Flame - GamProducts) | 0.162               | 0.191             |

Table 3. Dose and absorbance data for PRESAGE™

| Dose Gy | 0.1 | 0.3 | 0.6 | 1   | 3   | 6   | 10  | 30  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Absorbance(cm$^{-1}$) | 0.024 | 0.063 | 0.110 | 0.159 | 0.508 | 0.988 | 1.593 | 4.427 |

The most sensitive are the carbon iodide initiators followed by the carbon bromide and then the carbon chloride, which correlates with the bond energies of these compounds [4]. The photo reactivity of the dosimeter formulation is presented in Table 2.

The linearity of the radiochromic response in 2% LMG polyurethane formulation was studied from 10 cGy to 60 Gy. The data is presented in Table 3.

4. Discussion

There are seven common transparent plastics that are potential candidates for a dosimeter matrix and they are acrylics, epoxies, polycarbonates, polyesters, polystyrene, polyurethanes, and polyvinylchlorides. Polyvinylchlorides weren’t further considered since their $Z_{\text{eff}}$ values are not tissue substitutes with $Z_{\text{eff}}$ 14.2. The acrylates, polyesters, polystyrenes and polycarbonates were also dropped from further consideration due to the relatively high heat (>100°C) measured during their polymerization, which degrade leuco dyes. The remaining two plastics further studied were epoxies and polyurethanes and from these polyurethanes show the greatest versatility as a 3D dosimeter matrix by generating the least exotherm and the greatest dose sensitivity. The consequence of the lower exotherm has been that larger polyurethane dosimeters with diameters and heights of 14 cm have been manufactured.

Using a polyurethane formulation containing 2% LMG a radiochromic response at 630 nm was linear from 0.1 Gy to approximately 30 Gy with a slope of 0.16 cm$^{-1}$/Gy and with an error, $R^2$, of 0.9995. Above 30 Gy, transmission measurements were limited by spectrometer stray light. The lower limit of dose measurement is approximately 10 cGy, for a 1 cm pathlength.

When exposed to room light for 24 hr the optimal dosimeter background increased 1.373 cm$^{-1}$. The greatest inhibition to photoreactivity came from the use of colored lighting filters with the GAMTube Amber Flame (GET5355) with an increase in background of only 0.03 cm$^{-1}$ after 24 hr.
In summary, a polyurethane matrix with 2% LMG leuco dye containing a carbon halogen initiator is sensitive to high energy radiation and has a linear response to dose. However, this potential 3D dosimeter must be protected from UV and blue light.

5. References
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