Transactions of the Korean Nuclear Society Autumn Meeting
Gyeongju, Korea, October 27-28, 2016

Comparison between Two Bromine Containing Free Radical Initiators in PRESAGE® Dosimeter

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1. Introduction

PRESAGE® is an optically clear 3-D polyurethane dosimeter which contains a halogenated carbon as a free radical initiator and leucomalachite dye [1]. The initiator which contains the halogen-carbon bond produces free radicals upon irradiation and results in changing the optical density by oxidizing the leucomalachite green (LMG) dye. The change of the optical density is known to be linear with respect to the absorbed dose and the sensitivity is related to the carbon–halogen bond dissociation energy of the free radical initiator [2]. Although there are some studies regarding free radical initiators and dye materials [3], there's a lack of reports about the effect of other elements like LMG solvent which can be added when there's a difficulty mixing materials. Also, there are some studies about comparison between free radicals with different kind of halogen atoms [2] but there's a lack of studies of comparison between initiators with the same halogen atom.

In this experiments, two kinds of halocarbon free radical initiator with the same halogen atom (bromine) as well as the effect of the LMG solvent were studied to use the dosimeter as a therapeutic purpose. Effective atomic numbers were also calculated.

2. Materials and Methods

2.1. Chemical Formula for PRESAGE® Dosimeters

Four PRESAGE® formula were used in this experiment (Table I). All formula contained the same amount of leucomalachite green (2 wt%) and Dibutyltin dilaurate as a catalyst (0.05 wt%). The polyurethane resin precursors used in this study was Crystal Clear 200 (Smooth-On, Easton, PA USA).

Table I: Chemical formula of the PRESAGE® dosimeters

	Initiator	*LMG Solvent*
Formulation A	CBr_4 0.56 wt%	Cyclohexanone 7 wt%
Formulation B	CBr_4 0.5 wt%	Cyclohexanone 3 wt%
Formulation C	$C_2H_2Br_4$ 0.56 wt%	-
Formulation D	$C_2H_2Br_4$ 0.56 wt%	Cyclohexanone 3 wt%

2.2 Fabrication of PRESAGE® dosimeter

The fabrication process of PRESAGE® dosimeter was as follow.

The radical initiator and leucomalachite green dye were well mixed together. After that, they were put into the polyurethane resin precursor part A. In case of using crystal type radical initiator like CBr_4, LMG solvent is necessary to dissolve the LMG into polyurethane resin precursors. When they were well mixed together, the polyurethane resin precursor part B was mixed together. Finally, catalyst (in this study, Dibutyltin dilaurate) were added for the purpose of better polymerization, sensitivity and post-irradiation stability [4]. After that, the dosimeters inside the desired mold or cuvettes were placed in a pressure pot (60 psi) for 18-24 h to eliminate the air bubbles inside the dosimeters which can create error while dose measurement.

2.3. Effective atomic number calculations

The elemental composition of the Smooth-On Crystal Clear series is C: 63.3 %; H: 9.4%; N:5.0 %; O: 21.3 % [4]. This information was used to calculate the elemental compositions and effective atomic numbers.

The effective atomic numbers of each dosimeter were calculated using Mayneord equation [5].

$$Z_{eff} = \sqrt[2.94]{\sum_{i=1}^{n} a_i Z_i^{2.94}} \quad (1)$$

Where a_i is the fractional contributions of each element to the total number of electrons in the mixture and Z_i is the atomic number of each element.

2.4. Irradiation

For each formulation, the PRESAGE® cuvettes were irradiated to 1, 2, 3, 5, 10, 20, 30 Gy using X-RAD320 biological irradiator (Precision X-Ray Inc., USA) at 250 kVp, 15 mA, with a 2 mm Al filter and at 35 cm from the source with 10×10 cm^2 field size.

2.5. Absorbance measurement

The absorbance spectra were measured using a Perkin-Elmer Lambda 35 UV-vis spectrometer between wavelength of 500-700 nm. Four points along the length of the cuvette were measured and averaged to reduce any disturbance inside the cuvettes. To test the post-irradiation effect, absorbance was measured over 4 days.

All measurements were done in dark room and stored in a freezer and dark environment to avoid any thermal and UV contamination.

3. Results and discussion

3.1. Effective atomic number calculations

The calculated data are listed in Table II. In terms of effective atomic number calculated using Mayneord equation, all PRESAGE® formula showed similar values to water.

3.2. Absorption spectrum

Absorption spectrum for formulation B measured between the wavelength of 500-700 nm are plotted in Fig. 1. The maximum absorption occurred at 629 or 630 nm. It can be seen that the maximum peak values are increased along with the exposed dose. All PRESAGE® used in this study showed the same trend.

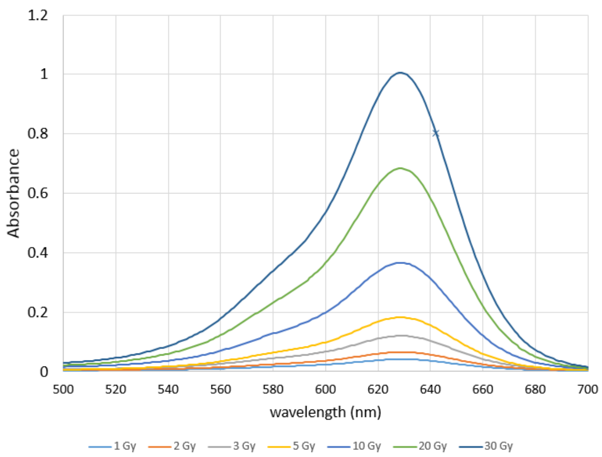

Fig. 1. Absorption spectra of the formulation B measured between the wavelength of 500-700 nm

Table II: Elemental compositions of the PRESAGE® dosimeters used in this study

	w_H (%)	*w_C (%)*	*w_N (%)*	*w_O (%)*	*w_{Br} (%)*	*w_{Sn} (%)*
Formulation A	9.32	6.34	5.05	20.72	0.58	0.01
Formulation B	9.32	63.43	5.05	20.72	0.50	0.01
Formulation C	9.32	63.43	5.04	20.75	0.52	0.01
Formulation D	9.32	63.42	5.04	20.74	0.53	0.01
H_2O	11.19	-	-	88.81	-	-

Table III: Effective atomic number of the PRESAGE® dosimeters used in this study

	Formulation A	*Formulation B*	*Formulation C*	*Formulation D*	*H_2O*
Z_{eff}	7.49	7.49	7.46	7.45	7.42

3.3. Calibration curve

The calibration curves within 2 hours after irradiation are plotted in Fig.2. The sensitivities of the formulation A, B, C and D are 0.0331 Gy^{-1}, 0.0329 Gy^{-1}, 0.087 Gy^{-1} and 0.082 Gy^{-1}. Although CBr_4 and $C_2H_2Br_4$ has a same amount of C-Br bond per a molecule, CBr_4 has slightly less molar mass (331.63 g mol^{-1}) than that of $C_2H_2Br_4$ (345.65 g mol^{-1}) which suggest that the number of C-Br bond of CBr_4 is slightly higher than that of $C_2H_2Br_4$ when they are same weight. But it cannot fully explain the 3~4 times increment of sensitivity when CBr_4 is used instead of $C_2H_2Br_4$.

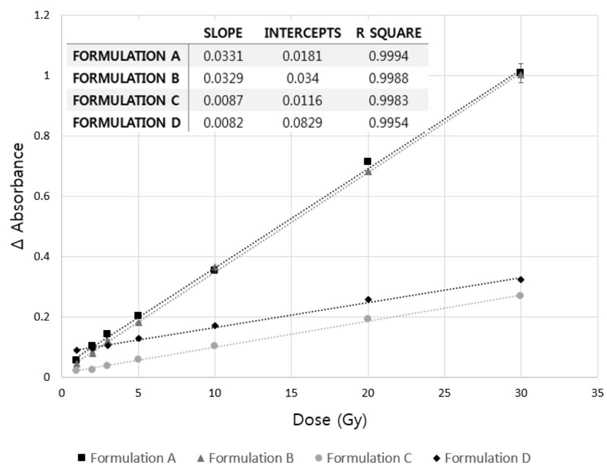

Fig. 2. Fitting curve for PRESAGE® dosimeter 2 hrs after irradiation

Meanwhile, there is no significant effect of adding LMG solvent, cyclohexanone, on initial sensitivity although the overall measurements were decreased nearly half in the case of PRESAGE® with solvent and $C_2H_2Br_4$ (formulation D) when compared to the formulation C which had no solvent (Fig. 3). This may have been the measurement error in 0 Gy cuvette. All calibration curves showed high linearity (R^2>0.99).

3.4. Post-irradiation effect

The results of post-irradiation effect of cuvettes irradiated to 5 Gy are plotted in Fig. 3. The absorbance of the CBr_4 containing PRESAGE® (formulation A and B) decreased rapidly (23.16 % for formulation A, 28.46 % for formulation B) before they were stabilized while $C_2H_2Br_4$ containing PRESAGE®, formulation C and D, changed 12.14 % and 12.68 %. All PRESAGE® formula showed high linearity (R^2>0.99) over time except formulation B where R^2 was continuously decreased after irradiation (Table. III).

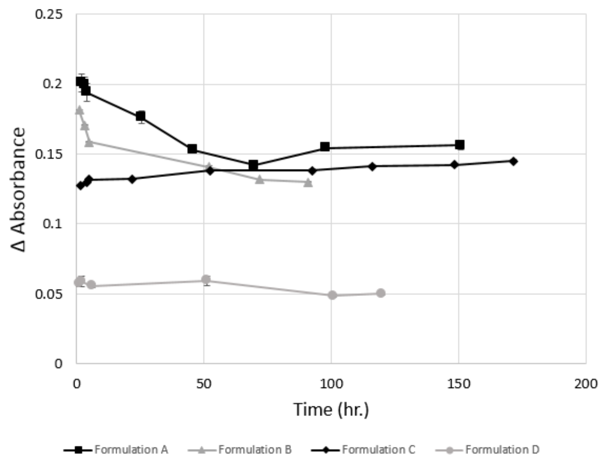

Fig. 3. Post-irradiation effect of the PRESAGE® dosimeters irradiated to 5 Gy

Table IV: Fitting curve data for the PRESAGE® dosimeters

Formulation A					
Time after irradiation(hr.)	**2**	**25.5**	**46**	**98**	**151**
Slope	0.033	0.024	0.017	0.015	0.015
Intercept	0.1034	0.051	0.056	0.074	0.077
R^2	0.999	0.998	0.994	0.998	0.997
Formulation B					
Time after irradiation(hr.)	**1**	**5**	**52**	**72**	**91**
Slope	0.033	0.024	0.018	0.016	0.016
Intercept	0.018	0.035	0.045	0.046	0.048
R^2	0.999	0.995	0.989	0.987	0.985
Formulation C					
Time after irradiation(hr.)	**1.5**	**22**	**52.5**	**148.5**	**171.5**
Slope	0.008	0.009	0.009	0.009	0.009
Intercept	0.083	0.091	0.091	0.096	0.097
R^2	0.996	0.999	0.999	0.999	0.999
Formulation D					
Time after irradiation(hr.)	**1**	**2**	**6**	**51**	**101**
Slope	0.009	0.009	0.009	0.008	0.008
Intercept	0.012	0.013	0.013	0.019	0.008
R^2	0.998	0.995	0.998	0.995	0.999

The use of cyclohexanone as a LMG solvent makes the fabrication process easier because it can dissolve LMG easily instead of stirring the mixture for a few minutes. The results showed that different amount of cyclohexanone have negligible effect on the sensitivity of the dosimeter while it seems to affect the post-irradiation response when it is used especially with the CBr_4. To figure out the effect of the LMG solvent, further study will be needed.

CBr_4 can be used as an initiator in the PRESAGE® dosimeter but it was highly variable until it was stabilized, which takes 90-100 hours after irradiation. The variation was less when $C_2H_2Br_4$ was used instead of CBr_4. Hence, $C_2H_2Br_4$ is more appropriate when it needs to be measured short time after irradiation.

Whereas, dosimeter with CBr_4 was about maximum four times more sensitive than the one with $C_2H_2Br_4$. The increment of sensitivity required no additional effective atomic number. When a fast reading equipment which takes only few minutes are available, PRESAGE® dosimeter with CBr_4 can be used as a high sensitive dosimeter.

4. Conclusions

The initiators with the same halogen atom, CBr_4 and $C_2H_2Br_4$, reacted totally differently. CBr_4 was more sensitive to the radiation and emitted maximum 4 times more free radicals upon irradiation with no additional effective atomic number but the absorbance after irradiation was highly variable with time. For stable measurement, $C_2H_2Br_4$ would be more appropriate as a free radical initiator. However, CBr_4 can be considered as a high sensitive dosimeter. Other components like LMG solvent may affect the performance of the dosimeter.

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