Influence of the components of a radiochromic PVA – Iodide gel dosimeter on the optical dose response

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Abstract. A novel radiochromic gel dosimeter based on a poly(vinyl alcohol)-iodide complex (PVA-I) has been developed with the aim of using it in optical computed tomography (CT). The PVA-I gel dosimeter exhibits excellent characteristics such as high sensitivity, dose rate independence, a wide dose range, and especially reusability. The standard PVA-I gel dosimeter is composed of poly(vinyl alcohol) (average degree of polymerization 1000 and degree of saponification 88 mol%), iodide (potassium iodide), reducing sugar (fructose), gelling agent (gellan gum), and water. In this study, the influence on dose response is investigated upon substitution of the components by PVAs with different degrees of polymerization (500, 1500, 3500) and saponification (80 mol%, 98 mol%), different iodide salts (LiI, NaI, NH4I), and different reducing sugars (glucose, maltose, lactose). The results show that these substitutions have little effect on the dose rate dependence, while the iodide salt affects the sensitivity.

1. Introduction
In the past decade, various radiochromic gel dosimeters employing radiation sensitive dyes have been studied. Among them, the most typical dye gel dosimeter is a micelle gel dosimeter using Leuco Malachite Green [1] or Leuco Crystal Violet [2] as the dye. Others using a genipin gel [3], a tetrazolium salt gel [4], and more have also been reported.

Recently, a radiochromic gel indicator based on a poly(vinyl alcohol)-iodide complex (PVA-I) was reported by Sunagawa et al. [5, 6]. The indicator changes from colorless to red by radiation with high sensitivity but is also decolored by heating in the presence of a reducing sugar, thus being reusable. We have applied this system to a novel three-dimensional (3D) radiochromic gel dosimeter [7]. The PVA-I gel dosimeter investigated in our previous work is composed of partially saponified PVA (degree of saponification (DS) of 86-90 mol%, average degree of polymerization (DP) 1000), iodide (potassium iodide, KI), reducing sugar (fructose), gelling agent (gellan gum, GG), and distilled water. The reactions in this system are represented by the following scheme.

1) $\text{H}_2\text{O} \rightarrow \text{R}^\cdot$ (Radiolysis)
2) $3\text{I}^- (+ \text{R}^\cdot) \rightarrow \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$ (Oxidation)
3) $\text{PVA} + \text{I}_3^- \rightarrow \text{PVA-I}$ (Complexation, colored)
4) $\text{PVA-I} \rightarrow \text{PVA} + \text{I}_3^-$ (Dissociation, decolored)
5) $\text{I}_3^- (+ \text{RS}) \rightarrow 3\text{I}^-$ (Reduction)
An iodide ion is oxidized by the radical ($R\cdot$) generated by the radiolysis of water, creating an iodide molecule ($I_2$). Although the iodide molecule is insoluble in water, the triiodide ion, which is soluble, is immediately formed upon binding with another iodide ion. The triiodide ion forms a complex with the maldistributed group of a residual acetyl group in PVA, resulting in red colorization. This PVA-I complex dissociates to give PVA and a triiodide ion upon heating. Subsequently, the triiodide ion is reduced to mono-iodide ions in the presence of a reducing sugar (RS), resulting in decolorization.

Besides its reusability, the PVA-I gel dosimeter also has some excellent characteristics such as high sensitivity, dose rate independence, a wide dose range, and more [7]. In the present study, the influence on the dose response was investigated upon substitution of the various components (except for the gelling agent) with a different iodide salt (LiI, NaI, NH$_4$I), a different reducing sugar (glucose, maltose, lactose), and PVAs with different DP (500, 1500, 3500) or DS (80 mol%, 98 mol%).

| Table 1. The components of the PVA-I gel dosimeter prepared in the present work. Each component of the standard gel dosimeter (marked in bold) was substituted one at a time. M is molarity (mol/1000gH$_2$O). |
|---|
| **Base solution** |
| PVA | Degree of polymerization | 500 | 1000 | 1500 | 3500 |
| Gellan gum | Degree of saponification (mol%) | 80 | 88 | 98 |
| Water | | | | | 1.0 wt% |
| | | | | 0.4 wt% |
| | | | | 98.6 wt% |
| **Additives** |
| Iodide salt | LiI | NaI | KI | NH$_4$I |
| Reducing sugar | glucose | fructose | maltose | lactose |
| | 100 mM | | 100 mM |

2. Materials and methods

2.1. Gel preparation
The compositions of the PVA-I gel dosimeters prepared in the present work are shown in Table 1. All reagents were purchased from Wako Pure Chemical Industries Ltd (Japan). Solutions of each type of 10 wt% PVA and a solution of 0.8 wt% GG were prepared in advance and mixed with distilled water at room temperature to prepare base solutions containing 1 wt% PVA and 0.4 wt% GG. After heating the base solution to 60°C while stirring, an iodide salt and a reducing sugar were added. The resulting solution was subdivided into PMMA cuvettes (4.5 mL, 1 cm path length) and cooled to room temperature. Before irradiation, the samples were initialized by annealing them at 45°C for 12 hours in an incubator.

2.2. Irradiation
Sample irradiation was performed using a 6 MV photon beam of a medical linear accelerator (Varian/BrainLAB Novalis Tx, USA). Samples were irradiated at a depth of 5 cm in a tough water phantom at room temperature. The axis of the cuvette was perpendicular to the beam. An irradiation field size of $15 \times 15$ cm$^2$ was used with a 100 cm source-to-axis distance (SAD). The beam was delivered to the cuvettes up to 20 Gy, with the dose rate fixed at 600 cGy/min. Different dose rates (100, 200, and 400 cGy/min) at 10 Gy were also utilized to investigate the dose rate dependence.

2.3. Measurement
Absorption spectra of the samples were measured one day after being irradiated at different doses. The measurements were performed at room temperature using an UV-Vis spectrometer (UV-1600PC, SHIMADZU, Japan) over the wavelength region of 350–800 nm. Absorbance (Abs) was calibrated using a reference cuvette filled with distilled water. The change in the absorbance ($\Delta$ Abs) was obtained by subtracting the absorbance value of the non-irradiated sample from that of the irradiated sample:
\[ \Delta \text{Abs} = \text{Abs}(i) - \text{Abs}(n) \]  

where Abs(i) and Abs(n) are the absorbances of the irradiated and non-irradiated samples, respectively.

Figure 1. PVA-(Na)I gel samples irradiated up to 20 Gy.

Figure 2. Absorption spectra of PVA-(Na)I gel samples irradiated up to 20 Gy.

3. Results and Discussion

Figure 1 shows the PVA-I gel dosimeters as they were irradiated up to 20 Gy. As the absorbed dose increased, they gradually changed from colorless to red. Figure 2 shows the absorption spectra of the gels. Single peaks were almost exclusively observed, centered around 490 nm.

3.1. Dose-absorbance responses

3.1.1. Degrees of polymerization (DP) and saponification (DS) of PVA

Figure 3 (left) shows the dose-absorbance responses at 490 nm of the PVA-I gel dosimeters fabricated with PVAs with different degrees of polymerization and saponification. The results show that the sensitivity of the PVA-I gel dosimeters was almost independent of the DP, although the sensitivity of the dosimeter incorporating PVA with a DP of 3500 was somewhat low. The sensitivity of the dosimeter using PVA with a DS of 80 mol% was slightly higher than it was for the devices employing the other PVAs. In the PVA-I gel dosimeter using the PVA with a DS of 98 mol%, the peak was not observed. These results are consistent with those of the experiment using partially saponified PVA and an iodine-potassium iodide (KI/I₂) solution [8]. In addition, the PVA-I gels with DS of 80 mol% or DP of 3500 exhibited higher viscosities than the other gels. Therefore, it was easier to prepare a gel dosimeter using PVA with a DP of 500–1000 and a DS of 88 mol%.

3.1.2. Reducing sugar

Figure 4 (left) shows the dose-absorbance responses at 490 nm of the PVA-I gel dosimeters incorporating different reducing sugars. The sensitivity of the dosimeter containing fructose was somewhat higher than it was for the others. This may be due to the ketose-aldose equilibrium of fructose, although the cause has not been confirmed.

3.1.3. Iodide source

Figure 5 (left) shows the dose-absorbance responses at 490 nm of the PVA-I gel dosimeters using different iodide salts. The sensitivity of the dosimeter containing KI was the highest. The induction region in the lower dose range was observed for the dosimeter containing LiI. The compositions of the dosimeters being compared in this section are almost the same, differing only in the counter cations (K⁺, Na⁺, Li⁺, NH₄⁺). These cations essentially act as physical cross-linkers for the gelation of gellan gum. However, it is interesting that the influence of the salt on the dose sensitivity was larger than the influence of the other components. The ionic radius, hydration force, or pH may all affect the structure of the maldistributed group of the residual acetyl group in PVA, which forms the complex with iodide.
3.2. Dose rate dependence

Figures 3 (right), 4 (right), and 5 (right) show the dose rate dependencies of the absorbance at 10 Gy in the PVA-I gel dosimeters containing each corresponding component. It is seen that the dose rate independence of the standard PVA-I gel dosimeter was not affected by substitution of the different components.

**Figure 3.** Dose-ΔAbs (at 490 nm) responses (left) and the dose rate dependence of the absorbance at 10 Gy (right) in the PVA-I gel dosimeters containing PVA with different DPs and DSs. KI and fructose are used as a source of iodide ions and a reducing sugar, respectively. The data points of DP=500, 1000, 1500, and DS=88mol% almost overlap each other.

**Figure 4.** Dose-ΔAbs (at 490 nm) responses (left) and the dose rate dependence of the absorbance at 10 Gy (right) in the PVA-I gel dosimeters containing a different reducing sugar. PVA (DP=1000, DS=88 mol%) and KI are used as a PVA and a source of iodide ions, respectively. The data points of glucose, maltose, lactose almost overlap each other.
Figure 5. Dose-ΔAbs (at 490 nm) responses (left) and the dose rate dependence of the absorbance at 10 Gy (right) in the PVA-I gel dosimeters containing a different iodide salt. PVA (DP=1000, DS=88 mol%) and fructose are used as a PVA and a reducing sugar, respectively.

4. Conclusion
In this study, the influence of the chemical components on the dose response behavior of a novel radiochromic gel dosimeter based on a poly(vinyl alcohol)-iodide complex was investigated. Substitution of the components did not inhibit the favorable characteristics of this dosimeter, except for decreasing the sensitivity of the gel dosimeter containing LiI. Based on these results, the standard PVA-I gel dosimeter is expected to be a more useful dosimetric tool in radiotherapy. However, further optimization of the composition and evaluation of its fundamental characteristics, such as thermal and spatial stabilities, are needed. Efforts to address these topics are currently underway.

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