Radiation induced degradation of rhodamine 6G and 7-Diethylamino-4-methylcoumarin in nano-clay gel for use in dosimeter

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Abstract. Rhodamine 6G (R6G) and 7-diethylamino-4-methylcoumarin (7D4MC) were applied to a nanoclay gel dosimeter based on radiation-induced degradation. The radiological properties were evaluated under X-ray irradiation. The fluorescent dyes showed linear degradation with an increase in dose. In addition, the distribution of fluorescence induced by inhomogeneous irradiation was maintained for two months and a suppressed diffusion of the fluorescent dyes in the gel matrix was observed.

1. Introduction
The 3D gel dosimetry [1] is a useful tool for dose verification in advanced radiotherapy because a gel dosimeter can be used as phantom in the same way as in an actual treatment chain of radiotherapy [2, 3]. Several studies have contributed to the development of gel dosimeters using fluorescence spectroscopy [4-8]. Recently, we reported a nanoclay gel-based radio-fluorogenic gel (NC-RFG) dosimeter [9]. These gel dosimeters use a chemical compound, known as a radio-fluorogenic probe or a fluorescence probe, in which a fluorescent dye is produced when a non-fluorescent dye reacts with radicals formed via the radiolysis of water.

Radiation-induced degradation of fluorescent dyes is also used in dosimeters, particularly for high-dose dosimetry in the liquid state [10, 11]. When rhodamine 6G (R6G) is used as a fluorescent dye, a gelatin-based gel dosimeter shows a good dose linearity within 0-200 Gy [12].

This study reports on a nanoclay-based gel dosimeter that uses the radiation-induced degradation of a fluorescent dye. Nanoclay is easily dispersed in water without heating and forms thixotropic gel. Several kinds of gel dosimeters containing nano-sized particles have been discussed for Fricke gels [13-19] and for polymer gels [20, 21]. In the initial investigations, R6G and 7-diethylamino-4-methylcoumarin (7D4MC) [22], are explored. The fluorescence of these dyes degrades with increasing radiation dose. In addition, the distribution of fluorescence induced by inhomogeneous irradiation is maintained.

2. Material and methods
R6G and 7D4MC were used as the fluorescent dyes in this study. On the basis of a previously reported method [9, 16], we prepared gel samples containing 1.5-wt% nanoclay (Laponite XLG) and 1-µM fluorescent dye, which were sealed into 5-mL vials. Gel samples having an increased clay concentration
up to 2.5 wt% were prepared and sealed into Petri dishes (2 cm high and 9 cm in diameter) for 2D measurements. Table 1 summarizes the details of these preparation conditions. The prepared samples were irradiated using an industrial X-ray machine (250 kVp, 8 mA, with a 1-mm-thick Al filter; Rigaku Radioflex 250CG, Japan) at a dose rate of 1.64 ± 0.01 Gy/min, determined using aqueous Fricke solution dosimetry. Two or three days post irradiation, fluorescence measurements of the irradiated samples were done using a F-4500 Spectrofluorometer (Hitachi, Japan). Two months (58 days) after the inhomogeneous irradiation, 2D distribution measurements were conducted using a digital camera in a dark box under 365-nm excitation.

Table 1. Chemical composition of the fluorescent dye gels.

| No | Fluorescent dye | Clay [wt%] | Dose [Gy] | Fluorescent measurement [nm] |
|----|----------------|------------|-----------|-----------------------------|
| 1  | R6G            | 1 µM       | 0–50      | 500                         | 562 | 2.5/5.0 |
| 2  | 7D4MC          | 1 µM       | 0–40      | 394                         | 448 | 2.5/5.0 |
| 3  | 7D4MC          | 0.25 µM    | 0, 30, 60 | 365 (peak)                 | --  | Digital Camera |

3. Results and discussion

Fig. 1 shows the radiation-induced degradation in the fluorescence properties of R6G. By X-ray irradiation, degradation of a peak at 555 nm was observed in the excitation spectra (dashed lines) and a peak at 562 nm decreased in the fluorescence spectra (solid lines). A small Stokes shift (the difference between the excitation and emission maxima) compared to a R6G solution without clay was evident, and a red shift in the excitation and emission spectra was observed upon the addition of the nanoclay (the red and black dot-line in Fig. 1 (A), respectively). In contrast, good linearity in the differential fluorescence intensity with increasing dose was observed within 0–50 Gy under 500-nm excitation.

Figure 1. (a) Fluorescence properties of 0.1-µM R6G in 1.5-wt% clay before and after irradiation. Dashed and solid lines show the excitation and fluorescence spectra, respectively. Red and black dot-line show the excitation and fluorescence spectra of R6G in the water, respectively. (b) Dose dependence of fluorescence intensity at 562 nm using 500-nm excitation light.
In the case of 7D4MC, the fluorescence intensity also showed a linear decrease with increase in dose within 0-40 Gy (Fig. 2). In Fig. 2(a), degradation of a peak at 394 nm was observed in the excitation spectra by X-ray irradiation, whereas a peak at 448 nm decreased in the fluorescence spectra.

From Fig.1(b) and Fig.2(b), the radiolytic decomposition yields of the fluorescence dyes were roughly estimated from the ratio of degradation from the initial concentration (1 µM) as \( G(-R6G) = 0.00385\pm0.0001 \mu M/J \) and \( G(-7D4MC) = 0.016\pm0.001 \mu M/J \). The radiolytic decomposition yield of 7D4MC is three times higher than that of R6G under the same experimental conditions. In addition, the large Stokes shift of 7D4MC (54 nm) is convenient to reduction of noise from excitation light in the case of evaluation of 2 or 3D fluorescence measurement.

An aqueous R6G solution shows a high radiolytic decomposition yield of 0.3 \( \mu M/J \) using 1 to 0.1-mM R6G and 1-M ethyl alcohol [10]. This value is 80 times higher than that of R6G using a nanoclay gel. In contrast, the sensitivity of the gelatin-based R6G gel was approximately 0.0006–0.003 \( \mu M/J \), which depended on the concentration of inorganic ion radiosensitizer [12], and were of the same order as the results obtained using the nanoclay gel. Detailed discussion on the differences in yield require further experiments concerning the concentration dependence of the dyes [10], pH dependence [11], and clay effects [22].

An improvement in sensitivity is required for the use of 3D gel dosimetry in radiation therapy. For example, a nanoclay-based RFG is reported for doses within 0-5 Gy [9], which is several tens of times more sensitive than the results reported herein. Since sensitivity of radiation-induced fluorescence dye degradation is dependent on the ratio of the change in the total intensity, low sensitivities were shown than the RFG, if the measured yields by the reaction with water radiolysis radicals is the same as that in the RFG.

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In Fig. 3, a nanoclay gel with 2.5-wt% clay and 0.25-µM 7D4MC was irradiated with 15 and 30 min irradiation time that are roughly equivalent to 30 and 60 Gy, respectively. This figure was obtained using a digital camera placed in a dark box using a 365-nm excitation light, two months after irradiation. We
consider that the diffusion of 7D4MC is almost suppressed via adsorption of the nano-sized clay because we previously observed diffusion in a gel using anionic fluorescent dyes, such as fluorescein, uranine, and aromatic carboxylic acids (the details are not shown herein). In addition, the diffusion suppression of cationic substance in nanoclay gel was previously reported [14-16].

4. Conclusion
We reported a nanoclay gel dosimeter that utilized the radiation-induced degradation of fluorescent dyes. A gel using R6G or 7D4MC showed a linear response across the radiation dose range of 0-50 Gy. The diffusion of 7D4MC was suppressed since the dye distribution was maintained for two months after irradiation. The development of a 3D evaluation method of a fluorescence gel dosimeter is ongoing.

5. Acknowledgments
This study was supported by MEXT of JAPAN, KAKENHI Grant Number JP17K07013. We thank S. Hase, A. Kato and N. Sato (Kitasato Univ.) for experimental support.

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Figure 3. Irradiated nanoclay gel containing 7D4MC with doses 30 and 60 Gy.
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