Clear micelle gel dosimeter with nanoclay

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Abstract. We built a clear micelle gel dosimeter with nanoclay. Jordan et al. reported that Laponite RD clay nanoparticles when added to radiochromic leucomalachite green micelle gels eliminate diffusion and increase the dose sensitivity by roughly ten folds. However, owing to the cloudiness of the sample, there was a problem in reading the optical computed tomography (CT). In this study, we constructed a nanoclay-added micelle gel dosimeter by changing the type of gelatin. As a result, in addition to yielding a clear gel and making the optical CT readable, diffusion and temporal stability were improved more than the gel without using nanoclay, and the dosimeter showed the same level of sensitivity and diffusion as the one based on Laponite-added micelle gel reported by Jordan et al.

1. Introduction

Radiochromic gel dosimeters - micelle gel dosimeter, polymer gel dosimeter, and Fricke gel dosimeter - are one of the promising tools for verification of three-dimensional (3D) dose distribution [1]. Micelle gel dosimeter has several advantages over other types of dosimeters, such as, no or low diffusion, insensitivity to oxygen, lower toxicity, and suitability for optical computed tomography (CT) read-out. Such dosimeters based on both leucocrystal violet (LCV) and leucomalachite green (LMG) have been reported [2, 3]. However, dose sensitivities of these gels are low. To resolve this problem, addition of clay to radiochromic micelle gel has been studied. It has been reported by Jordan et al. that clay nanoparticles eliminate diffusion and increase dose sensitivity [4]. However, owing to the cloudiness of the sample, there was a problem in reading the optical CT.

The aqueous solution with nanoclay is transparent, and a high concentration solution with nanoclay directly forms a colorless gel [5]. It has been reported by Jordan et al. that, when preparing micelle gel dosimeter by adding Laponite RD clay nanoparticles, the micelle gel produces scattering signals. The more the number of scattering signals, the more is their influence, as seen in a polymer gel dosimeter. This influence cannot be ignored and it is considered that this might interfere with the measurement of...
an accurate 3D dose distribution, resulting in, for example, observation of cupping artifact [6]. In this study, in order to prepare a new micelle gel dosimeter by adding nanoclay and with the aim of obtaining a clear read-out, we changed the type of gelatin, and analysis of the gelatin was conducted to determine its influence on the gel dosimeter. Moreover, we investigated the sensitivity, diffusion, and temporal stability of this gel after subjecting it to X-ray irradiation.

2. Materials and methods

2.1. Gel fabrication
In this study, LCV (Wako Pure Chemical Inc., Japan) was used as a dye for radiochromic micelle gel. We used two types of gelatin: one was procured from Sigma-Aldrich (porcine, 300 bloom, USA), which was used in previous reports, and another was the guaranteed reagent of gelatin supplied by Nacalai Tesque Inc. (cattle bones, 150 bloom, Japan). The gel formulation comprised of 5% gelatin, 0.16% Laponite, 0.3 mM LCV, 50 mM dichloromethane, and 50 mM Triton X-100. Laponite XLG (BYK japan KK) was added to water and stirred to form a clear colorless solution in an oil bath at 50°C. The gelatin was slowly added to the Laponite solution and stirred in the same condition for 1 h. After the gelatin dissolved, the solution was cooled at 35°C. The dye was added to dichloromethane and mixed under light shielding. The dye solution was poured into Triton X-100 (Alfer Aesar, USA) and stirred at room temperature. The gelatin solution was added slowly to the surfactant solution and poured into 1-cm PMMA cuvettes or polyethylene terephthalate jars (900 mL) supplied by Modus Medical Devices. The samples were stored at 4°C for gelation.

2.2. Gelatin analysis
For investigating the composition of the two types of gelatin, element analysis (Elementar, Germany) and amino acid analysis using HPLC were carried out.

2.3. Irradiation
The samples were irradiated by 10-MV X-rays from a linear accelerator (Clinac iX Linear accelerator, Varian). For studying the sensitivity, some of the cuvettes were irradiated at 0–10 Gy. Additionally, another LCV sample was irradiated with 1000 MU (10 Gy) at the half-beam irradiation field with equal power of the upper and lower irradiation.

![Figure 1. Right: 1-cm PMMA cuvettes irradiated by X-rays. Left: polyethylene terephthalate jars (900 mL) irradiated by X-rays.](image)

2.4. UV-vis absorption measurement
For investigating the sensitivity and scattering signals, all the irradiated cuvettes were studied using UV-vis absorption spectrometer (JASCO, Japan). The reference was measured using water.
2.5. Optical CT scanning
Optical CT scanning was conducted with a commercial optical cone-beam scanner, model Vista 15 from Modus Medical Devices. In all the measurements, the reference and data scans were taken with 590 nm and 633 nm LED illumination, which is the maximum absorption wavelength of crystal violet (CV), and a 1024 × 768 pixel CCD camera. 342 image sets were reconstructed using a software provided by Vista15 scanner. The samples were stored at 4°C and brought to room temperature at the time of measurement.

3. Results and discussion
In the measurement of the scattering signals for UV-vis absorption, absorbance of the samples using the gelatin provided by Nacalai Tesque Inc. was weak at 590 nm, which is the maximum absorption wavelength of CV, and the values were similar to those without using nanoclay. On the other hand, the absorbance of the samples using the gelatin made by Sigma-Aldrich, which was used by Jordan et al., was generally stronger (figure 2).

As the measurement wavelength became shorter, the difference in absorbance between the two types of samples increased. These results indicated that the samples with gelatin provided by Nacalai Tesque Inc. have lower scattering signals than those by Sigma-Aldrich. The absorbance of pure gelatin samples of both Sigma-Aldrich and Nacalai Tesque Inc. were weak. A comparison of the photographs of the two samples suggest that the sample with gelatin provided by Sigma-Aldrich was more cloudy (figure 3).
These results indicate that difference in amino acid composition of the gelatins was caused by the cloudiness resulting from mixing with other substances (LCV, dichloromethane, and/or Triton X-100). The results of elemental analysis of gelatin (figure 4 left) and amino acid analysis (figure 4 right) are shown.

|        | C (%) | N (%) | H (%) | Others (%) |
|--------|-------|-------|-------|------------|
| Sigma Aldrich | 43.94 | 16.40 | 7.237 | 32.42       |
| Nacalai Tesque | 44.04 | 16.01 | 7.163 | 32.79       |

**Figure 4.** Results for two gelatins. Left: Elemental analysis and Right: Amino acid analysis.

The elemental analysis showed no significant difference between the two types of gelatins. Moreover, there is a possibility that the method of fabrication and type of nanoclay added also affect the cloudiness. In amino acid analysis as well, there were no considerable differences between the two types of gelatins in terms of the constituent amino acid type and its ratio. These observations suggest that impurities such as metals contained in gelatin and trace components derived from raw materials may affect the properties of the gel dosimeter.

Sensitivity to radiation was up to 10 Gy (5 Gy/min), as shown in figure 5. Compared with the case without nanoclay, the sensitivity was improved, and linearity was also observed.

**Figure 5.** Dose response of micelle gel dosimeters.

The sensitivity to X-rays obtained in this experiment was of about the same level as that reported by Jordan et al. In experiments with different dose rates (5 Gy/min vs 1.25 Gy/min), the absorbance of the samples with low dose rate was about 10% larger than that of the samples with high dose rate.

Half of the samples was irradiated in the vertical direction with respect to the container of the LCV sample, and the measurement was carried out by optical CT. The measured Vista CT at 590 nm was about 1.0 in the irradiated region, and it was practically readable. It was observed that the measurement
result at the center of the irradiation area was smaller than the calculated value of the treatment planning device (figure 6, top left). This is thought to be because of the influence of the dye’s scattering, but this issue is currently under investigation. On the other hand, the measured Vista CT at 633 nm was about 0.1 in the irradiated region (figure 6, bottom left). Because the influence of noise was large, the measured values of the irradiated region were observed to fluctuate, but roughly coincided with the calculated value of the treatment planning device.

![Figure 6](image_url)

**Figure 6.** Measurement result by optical CT at 590 nm (top) and 633 nm (bottom). Left: Comparison with calculated value. Right: Enlarged view of the center. Water was used as the reference.

In order to investigate the influence of diffusion, the data of 60 days after irradiation were investigated. The calculated profile is the result of simulation with the treatment planning system (Eclipse, VARIAN Medical Systems). The results in the vicinity of the boundary between the irradiated region and the nonirradiated region at the central part of the container measured at 590 nm and 633 nm were compared (figure 6, right). The data variation during this period was smaller than that when no nanoclay was used. Hence, dye diffusion was suppressed by the nanoclay.
4. Conclusion
A clear dye gel dosimeter with nanoclay was prepared. It was found that the gel prepared in this study had high transparency and sensitivity. In addition, it was found that the influence of diffusion of the coloring region and natural coloring of the gel was nominal, and that the dose distribution evaluation was not significantly affected until about 60 days.

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6. References
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