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Comparison of gamma ray and electron beam irradiations on the degradation of carboxymethylcellulose

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Abstract−Carboxymethylcellulose (CMC) is used for a variety of applications due to its superior properties of high viscosity at a low concentration. In this study, the difference between a gamma ray (GR) irradiation from Co-60 and an electron beam (EB) irradiation with 10 MeV Energy on the viscosity change in CMC solution was compared. At the same irradiation doses, the viscosity of the CMC solution was more severely decreased by GR. Electron spin resonance spectroscopy revealed that the radicals in the CMC were more generated by GR, but there was no difference in the Fourier transform infrared spectra of both irradiated CMC solutions. Also, the degree of substitution in CMC was not changed by both irradiation events. From these results, it can be concluded that EB irradiation could better minimize the decrease in the viscosity of the solution with CMC for the sterilization than GR.

Key words: Carboxymethylcellulose, Gamma Ray, Electron Beam, Viscosity, Electron Spin Resonance

INTRODUCTION

Carboxymethylcellulose (CMC) is a cellulose derivative with carboxymethyl groups bound to some of the hydroxyl groups of the glucopyranose monomers [1]. CMC is an industrially important cellulose derivative owing to its high viscosity at low concentration. Examples of industrial applications are found in the food industry as a thickener and a binder, in the oil industry as a lubricant for drilling, and in the cosmetic industry as a stabilizer and a binder [2]. Because of its non-toxicity, biodegradability, and biocompatibility, CMC gel has also been widely used as a carrier for a bone graft [3].

It has been found that the polysaccharides could be chemically modified by a radiation technique [4]. At a high concentration of CMC with a high degree of a substitution, CMC in a solution was cross-linked to form a hydrogel by the high dose of ionizing irradiation [5,6]. But, the small amount of CMC in the solution was degraded, resulting in a less viscous solution.

Recent advances in electron beam technology have made this mode of sterilization a worthy competitor to the traditional gamma processing techniques [7]. Electron beam irradiation has many advantages such as relatively short processing time, in-line processing, high effectiveness, low equipment cost, and an increased available energy.

There are several reports on the comparison of gamma ray and electron beam irradiations for CMC hydrogel formation at high CMC concentration [8]. But, in most cases, CMC has been used to enhance viscosity in the food and cosmetic industries at a low concentration; therefore, it is necessary to investigate the proper irradiation process for CMC solution with low concentration. Therefore, we studied the effect of irradiation sources on the changes of the viscosity of CMC and investigated the reason for the difference. Also, an experiment was performed to detect the change in the functional groups of CMC by irradiation.

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MATERIALS AND METHODS

1. Materials

Carboxymethylcellulose sodium salt (CMC) was purchased from SEAN Co., Ltd. (Chungnam, Republic of Korea). Its degree of substitution ranged from 0.9 to 1.05. For comparison purpose, the degree of substitution (DS) in CMC was determined by conductimetric titration according to Capitani et al. [9].

CMC solution was prepared by mixing the CMC with distilled water at the concentration of 3%.

2. Gamma Irradiation

CMC samples were irradiated in a cobalt-60 irradiator (point source AECL, IR-79, MDS Nordion International Co. Ltd., Ottawa, Ontario, Canada) at the Advanced Radiation Technology Institute, the Korea Atomic Energy Research Institute, in Jeongeup, Republic of Korea. The source strength was approximately 11.1 PBq with a dose rate of 10 kGy/h. The temperature of the irradiation room was 17 °C. Dosimetry was performed with 5 mm diameter alanine dosimeters (Bruker Instruments, Rheinstetten, Germany). The dosimeters were calibrated against an international standard set by the International Atomic Energy Agency (Vienna, Austria). The doses of 5, 10, 15, 20, 25, and 30 kGy were used in this study.

3. Electron Beam Irradiation

UELV-10-10S accelerator (NII EFA, Moscow, Russia) (energy 10 MeV, current 1 mA, output 570 kW) was used for the electron beam irradiation of the CMC solution. Irradiation was performed in the presence of air and the distance from the beam source to the sample was 50 cm. CMC solution was irradiated to 3 mm of thickness due to its low penetration.

4. Measuring the Viscosity

The viscosity of the CMC solution was measured by the Brookfield viscometer (DV-II pro, Brookfield Engineering Laboratories, MA) using spindle 7 at 1.8 rpm. The viscosity was determined at room temperature. The relative viscosity was determined as the percentage of the viscosity of the irradiated CMC solution to the unirradiated CMC solution at the same conditions. Each set of data represents the mean of three separate experiments.

5. Electron Spin Resonance (ESR) Analysis

The CMC samples were irradiated in the form of powder at liquid nitrogen temperature. The doses for gamma ray and electron beam irradiations were all 30 kGy. The ESR spectrum was measured at a microwave frequency of 9.18 GHz, a magnetic field of 347.05± 0.5 mT, a microwave power of 0.4 mW, modulation of 100 kHz, a time constant of 0.03 s, and a sweep time of 30 s by using an ESR spectrometer (JES-TE300, Jeol Co., Tokyo, Japan). At this time, the spectra of samples were scanned to record the signal intensity (peak-to-peak height).

6. Fourier-transform Infrared (FT-IR) Spectroscopy

The Fourier-transform infrared (FT-IR) spectra were acquired by using a Bruker Spectrometer VERTEX 70 (Bruker Optik, Ettlingen, Germany) at the wavelength region between 4,000 to 450 cm^{-1}. Samples were prepared as a thin film of the CMC mixed with KBr at polymer/KBr (w/w) ratio of 1/100. Obtained spectra were the result of 24 scans at the spectrophotometer resolution 8 cm^{-1}.

RESULTS AND DISCUSSIONS

1. Change of Viscosity by Ionizing Irradiation

Fig. 1 shows the relative viscosities of the gamma ray-irradiated and the electron beam-irradiated CMC solutions at various doses. The relative viscosities of CMC solutions were decreased by both types of irradiation. It has been generally reported that a radiation caused the degradation of polysaccharides by the cleavage of the glycosidic bond in cellulose backbone [4,10].

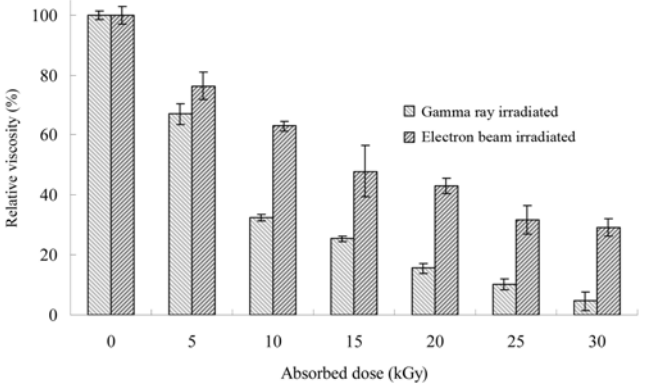

Fig. 1. The changes of relative viscosities of the gamma ray- and the electron beam-irradiated 3% CMC solutions at the various doses.

When the CMC solution was irradiated at the dose of 5 kGy, the relative viscosities of the CMC solutions irradiated with gamma ray and electron beam were decreased to 67% and 76% of the unirradiated control, respectively. At the dose of 10 kGy, the relative viscosity of gamma ray-irradiated CMC solution dropped to 33%, but the viscosity of electron beam-irradiated CMC was 63%. At the electron beam dose of 30 kGy, the relative viscosity of CMC solution irradiated with gamma ray was only 2.8%, but that of electron beam-irradiated CMC solution was 29.2%. At all of the doses tested in this experiment, the relative viscosities of the irradiated CMC solution were higher with electron beam than with gamma ray. To investigate this difference on the degradation of CMC in the solu-

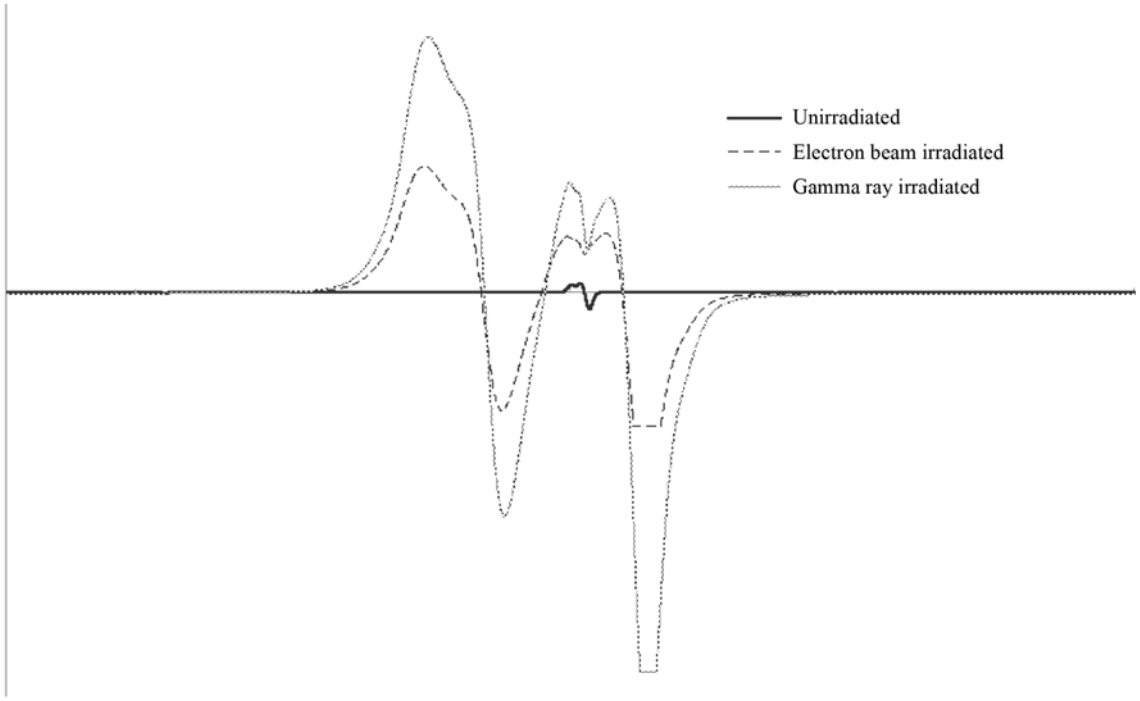

Fig. 2. ESR spectra of the unirradiated CMC and the gamma ray- and the electron beam-irradiated CMC samples at the dose of 30 kGy.

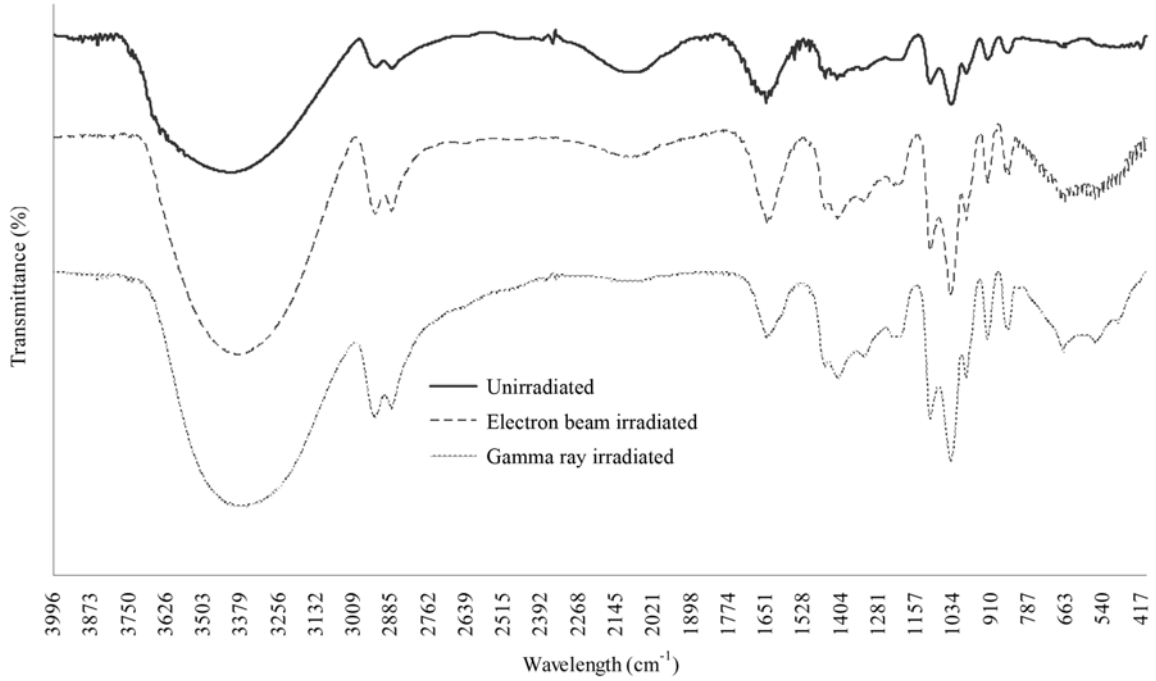

Fig. 3. FT-IR spectra of the unirradiated CMC and the gamma ray- and the electron beam-irradiated CMC samples at the dose of 30 kGy.

tion, the ESR experiment was carried out.

2. ESR Spectrum of CMC

Fig. 2 shows ESR spectra of unirradiated CMC and 30 kGy irradiated CMC samples by the gamma ray and the electron beam irradiations in the dry state. The spectra show the stable species that were specific of irradiated CMC [11]. The signals derived from radicals by the gamma ray and the electron beam irradiations were very similar, but the intensities of peaks were higher in the samples irradiated by the gamma ray. It meant that more free radicals caused severe degradation of CMC by the gamma irradiation. Wach et al. [8] reported that the ratio of degradation to crosslinking was significantly lower by an electron beam than by a gamma ray in CMC gel. At the same doses of the gamma ray and the electron beam irradiations, the dose rate (absorbed dose/time) is much higher in the electron beam irradiation system than in the gamma ray. Also, due to the low penetration of electron beam, radicals at higher density by the electron beam disappeared much faster. Ikada et al. [12] also observed this radical recombination in ultrahigh molecular weight polyethylene.

From this result, it could be reasoned that the lower viscosity of the gamma-irradiated CMC solution was caused by the higher concentration of free radicals.

3. FT-IR Spectra of CMC

Fig. 3 shows the FT-IR spectra in the range between 4,000 and 450 cm^{-1} for the unirradiated CMC and the gamma ray- and the electron beam-irradiated CMC samples at the doses of 30 kGy. The major bands of CMC indicate hydroxyl group around 3,400-3,600 cm^{-1}, carbonyl groups around 1,760 and 1,425 cm^{-1}, and ester group at 1,042 cm^{-1}, respectively [13]. As can be seen, the overall spectral pattern was not changed by the gamma ray- and the electron beam-irradiations, and additional bands did not appear. This indicated that the important functional groups were still present after the ionizing irradiations. Also, there was no difference between the gamma-irradiated and the electron beam-irradiated CMC solutions.

The degree of substitution in CMC was also not changed by the gamma ray and the electron beam irradiations (data not shown). These results supported that the functional groups of CMC were not changed by the irradiation.

CONCLUSIONS

These results show the difference between the gamma ray and the electron beam irradiations on the change of the viscosity of CMC solution. The gamma ray irradiation decreased the viscosity of CMC solution more severely than electron beam by higher concentration of free radicals. But, the functional groups and degree of substitution were not changed by both types of irradiation. These results will be helpful for the sterilization of products with CMC, and give another example explaining the difference between the gamma ray and the electron beam irradiations.

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