Molecular Weight Control of Chitosan Using Gamma Ray and Electron Beam Irradiation

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Abstract - Chitosan is a useful natural polymer material in many application fields such as biomaterials, water-treatment, agriculture, medication, and food science. However, the poor solubility limits its application. In this study, the effects of radiation on chitosan were investigated using gamma ray and electron beam irradiation. The chemical structure and molecular weight analysis show similar degradation effects of chitosan powder in both gamma ray and electron beam irradiation. However, the radiation irradiated chitosan in H_2O has a lower molecular weight, since the hydroxyl radicals attack the glycosidic bonds. This effect is more clearly shown in the electron beam irradiation results.

Key words : Chitosan, Gamma rays, Electron beam

INTRODUCTION

Chitosan has many unique properties such as non-toxic, biocompatible, and biodegradable. Thus, the importance of chitosan has been increasingly recognized in many application fields such as biomaterials, water-treatment, agriculture, medications, and food science (Kumar 2000; Jeun *et al*. 2009). Chitosan has been prepared from the *N*-deacetylation of chitin. It is the second most abundant natural polymer after cellulose. Chitosan consists of 2-amino-2-deoxy-(1→β) residues (D-glucosamine units) and contains no or a small amount of *N*-acetyl-D-glucosamine units.

Chitosan is difficult to dissolve in water and most organic solvents owing to its high molecular weight (Zhang *et al*. 2003). The poor solubility limits its application, especially in medicine and food science. Many researchers have studied the degradation of chitosan with various acids, such as hydrochloric acid, nitrous acid, phosphoric acid, and hydrogen fluoride to reduce its molecular weight. Degradation by gamma ray radiation has been recently investigated, since this technique provides a useful tool to separate oligochitosans (Choi *et al*. 2002; Hai *et al*. 2003; Kang *et al*. 2007). However, less attention has been paid to study on electron beam irradiation. An electron beam can provide faster processing than a gamma ray from ^{60}Co to irradiate the same radiation doses. It is also not needed to concern the radioactive waste. In this article, the radiation effects on chitosan were investigated using a gamma ray and electron beam at various dose rates. The changes in the chemical structure and molecular weight were investigated in detail.

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EXPERIMENTAL

1. Materials and radiation irradiation

A demineralized and deproteinized chitosan powder was used as supplied by Jakwang Co., Ltd., Korea. First sample series were fabricated by radiation irradiations on the chitosan powder using a gamma ray and electron beam. Gamma

ray irradiation was carried out at a dose rate of 10 kGy h^{-1} from a ^{60}Co source in an air atmosphere. Electron beam irradiation also was carried out at a dose rate of 10 kGy $scan^{-1}$ with a 10 m min^{-1} carrier velocity. The integral irradiation of the dose levels varied from 0 to 200 kGy. Second sample series were fabricated by radiation irradiation on the chitosan in water with different concentration, 2.5∼10 wt. %. Each radiation was irradiated on the second sample series with 100 kGy.

2. Measurement and characterization

The chemical structures of the radiation irradiated chitosan were characterized using a FT-IR (Brucker, Tensor 37) with transmittance mode in a wavenumber range of 400 to 4000 cm^{-1}. Gel permeation chromatography (GPC) of the irradiated samples was performed on a Waters GPC system equipped with a TSKgel G6000PWXL column (4.6 × 300 mm). The thermal behaviors were evaluated using the differential scanning calorimetry technique. DSC measurements were performed with a TA instruments DSC Q100 in a nitrogen atmosphere.

RESULTS AND DISCUSSION

1. FT-IR spectroscopy analysis

The FT-IR spectra of chitosan with radiation dose are shown in Fig. 1. Peaks appearing at 3,436, 2,925, 1,650, 1,074 and 1,020 cm^{-1} are assigned to O-H, C-H, N-H, C-N, and C-O-C, respectively. In both the electron beam and gamma ray irradiation on the chitosan powder, the C-H bonds increased gradually, and C-O-C bonds slightly decreased. These results show that the chitosan powder was degrad-

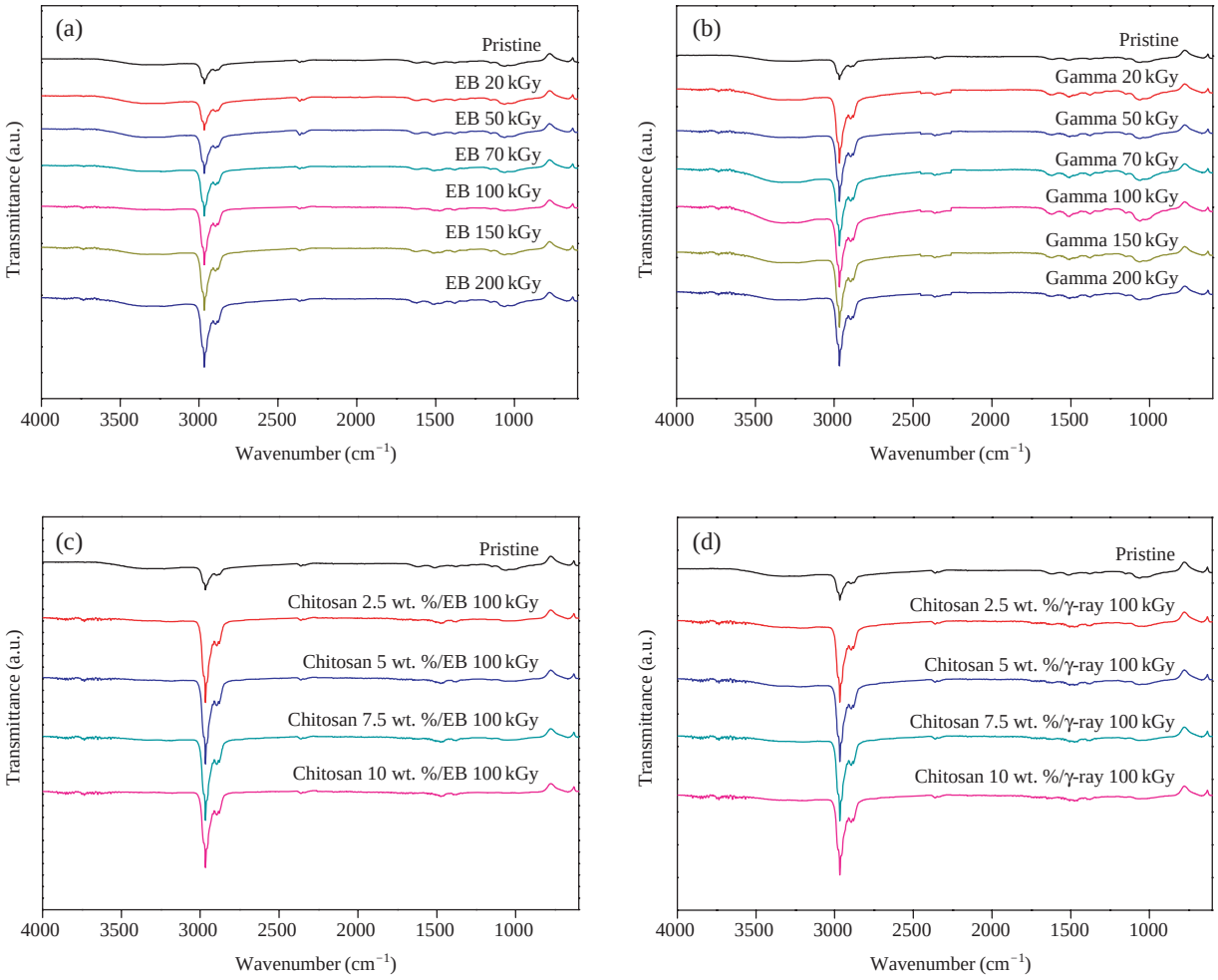

Fig. 1. FT-IR spectra of (a) electron beam irradiated, (b) gamma ray irradiated, (c) electron beam irradiated in H_2O and (d) gamma ray irradiated in H_2O.

ed by a destruction of β-1-4 glycosidic bonds (Gryczka *et al*. 2009). When the 100 kGy gamma ray was irradiated on the chitosan in water, C-H bonds are dramatically increased, and C-O-C peaks disappeared. Similar results were obtained in the case of the electron beam, and the C-H peaks are higher than in the gamma ray irradiation case.

The reason for the higher degradation of chitosan in water is the hydroxyl radicals created by a reaction with radiation and H_2O. When the radiation was irradiated on H_2O, the primary reaction can occur as follows:

$$H_2O \xrightarrow{h\nu} H_2,\ H_2O_2,\ e^-_{aq},\ H^\bullet,\ ^\bullet OH,\ H_3O^+$$

$$H^\bullet + H_2O_2 \longrightarrow H_2O + {}^\bullet OH$$

$$e^-_{aq} + H_2O_2 \longrightarrow {}^\bullet OH + OH^-$$

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^\bullet OH$$

$$R + {}^\bullet OH \longrightarrow R^\bullet + H_2O$$

$$R + {}^\bullet H \longrightarrow R^\bullet + H_2$$

$$R^\bullet \longrightarrow R_1 + R_2$$

These reactions lead to create the hydroxyl radicals, which can strongly attach the β-1-4 glycosidic bonds, and the degree of degradation was increased (Woods and Pikaev 1994).

2. Molecular weight

The change in molecular weight of chitosan powder at different radiation doses is illustrated in Fig. 2 base on the GPC analysis results. The molecular weight of chitosan powder was exponentially decreased with an increase in radiation dose from 15,000 g mol^{-1} (pristine) to 4,000 g mol^{-1} (200 kGy). Similar results were obtained in both cases of the gamma ray and electron beam irradiations. The decrease of molecular weight of chitosan powder is due to the degradation. Ershov *et al*. suggested the following degradation mechanism of irradiation on chitosan,

$$R\text{-}H \xrightarrow{h\nu} H^\bullet(C_4\text{-}C_6) + H^\bullet$$

$$R\text{-}H + H^\bullet \longrightarrow R^\bullet(C_1\text{-}C_6) + H_2$$

$$R^\bullet(C_1,\ C_6) \longrightarrow F_1^\bullet + F_2\ (\text{Scission})$$

$$R\text{-}NH_2 + H^\bullet \longrightarrow R^\bullet(C_2) + NH_3$$

where R-N and $R\text{-}NH_2$ are chitosan macromolecules, $R^\bullet(C_n)$ is a chitosan macroradical localized on a C_n carob atom, and $F_1^\bullet$, F_2 are fragments of the main chain after scission.

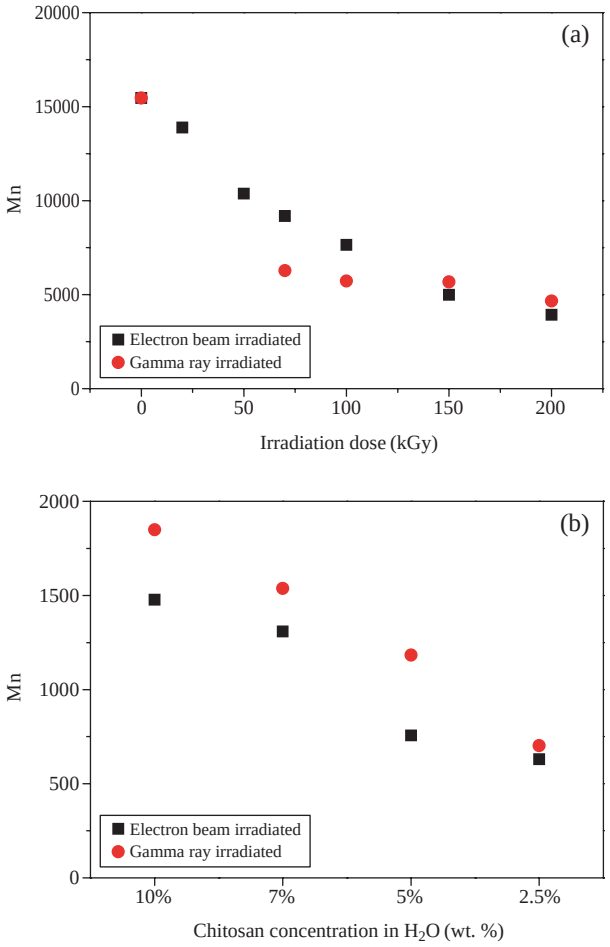

Fig. 2. The number average molecular weight of (a) radiation irradiated chitosan and (b) radiation irradiated chitosan in H_2O.

The second sample series show a lower molecular weight than first series at the same irradiation dose (100 kGy). As mentioned in the FT-IR analysis results, irradiated H_2O causes a degradation of the chitosan. Therefore, it is shown that the molecular weight depends on the chitosan concentration. The electron beam irradiation samples have a slightly lower molecular weight at the same chitosan concentration. It was thought that the electron beam irradiation produces much more hydroxyl radicals in a brief period of time, and consequently brings about a lower molecular weight.

3. Thermal behaviors

The spectra of radiation chitosan powder show two peaks in the DSC thermograms. One is a broad endothermic peak

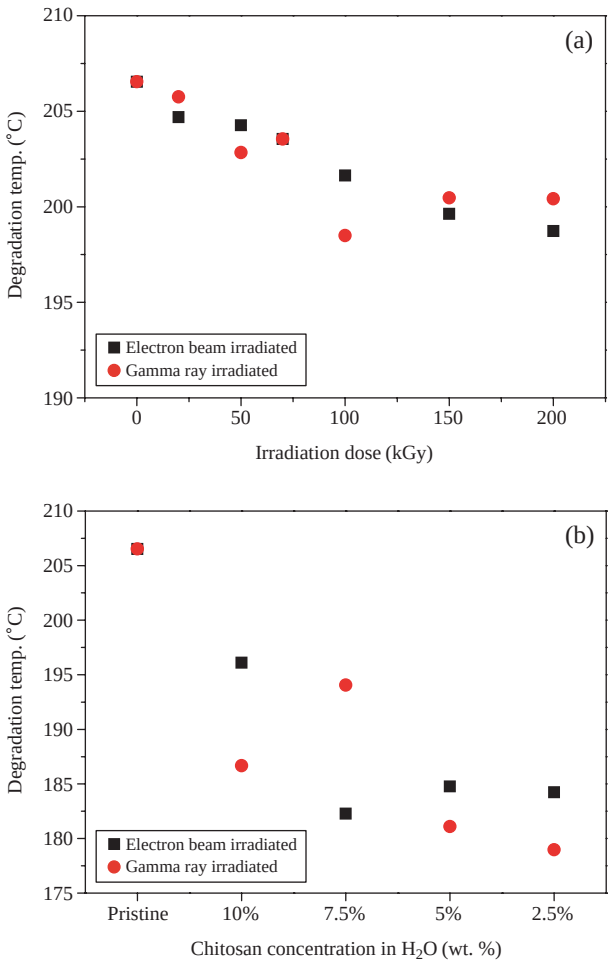

Fig. 3. Degradation peak point variation of (a) radiation irradiated chitosan and (b) radiation irradiated chitosan in H_2O.

at around 100˚C owing to the water vapor, and the other is a sharp exothermic peak at 207˚C from the chitosan degradation. The changes in exothermic peak points as a function of the radiation dose are shown in Fig. 3. With an increase in both the gamma ray and electron beam radiation doses, the points of exothermic peaks shift slightly to a lower temperature, from 207˚C to 200˚C. On the other hand, the exothermic peaks of radiation irradiated chitosan in H_2O dramatically shift to lower temperature to 180˚C. This result indicates that the hydroxyl radical from the water by radiation leads to a complete degradation of the chitosan.

CONCLUSION

This work describes investigations on the degradation of chitosan to enhance the water solubility by radiation, such as gamma rays and electron beams. The results of FT-IR and GPC analyses indicated that the chitosan powder was efficiently degraded by gamma ray and electron beam irradiation. The variations of the molecular weight showed the similar results at same irradiation dose in both cases. In addition, the chitosan can be more degradable in H_2O owing to the hydroxyl radical by radiation. The electron beam irradiated chitosan in H_2O has a lower molecular weight than the gamma ray irradiated chitosan. The electron beam irradiation can be a good chitosan degradation process in an industrial field.

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