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2.3 Radiation Processing of Natural Polymers using Low Energy Electron Beam

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Abstract

Radiation processing is widely used in Japan and the economic scale of radiation application amounted to about 71 b$ (ratio relative to GDP: 1.7 %) in total. It consisted of 60 b$ (85 %) in industry, 10 b$ (14 %) in medicine and 1 b$ (1 %) in agriculture. Irradiation using gamma-ray from ^{60}Co and electron beam is commercially used for the sterilization and modification of materials. Utilization of natural polymers by radiation has been investigated for recycling the natural resources and reducing the environmental pollution. Polysaccharides such as chitosan, sodium alginate, carrageenan, cellulose, pectin were easily degraded by irradiation and induced various kinds of biological activities, i.e. anti-bacterial activity, elicitor activity, plant growth promotion, suppression of environmental stress on plants. Radiation degraded chitosan was effective to enhance the growth of plants in tissue culture.

Low energy electron beam (EB) irradiation has a variety of applications and good safety. A self-shielded low energy electron accelerator system needs an initial investment much lower than a ^{60}Co facility. It was demonstrated that the liquid sample irradiation system using low energy EB was effective not only for the preparation of degraded polysaccharides but also for radiation vulcanization of natural rubber latex (RVNRL). Some carbohydrate derivatives, carboxymethylcellulose (CMC), carboxymethyl-starch and carboxymethyl-chitin/chitosan, can be crosslinked under certain radiation condition and produced the biodegradable hydrogel for medical and agricultural use. Treatment of soybean seeds by low energy EB enhanced the growth and the number of rhizobia on the root.

1. Introduction

A new project on "Application of Electron Accelerator" was proposed as an FNCA (Forum for Nuclear Cooperation in Asia) project. The objective of the project is to develop new technology of low energy electron beam (EB) irradiation system that has a variety of applications and good safety features, and to demonstrate its application. A self-shielded low energy accelerator system needs an initial investment much lower than a ^{60}Co facility. Its operation is simple and safe. The system can be applied in various fields such as radiation processing of natural resources, environmental conservation, etc.

An economic scale of "utilization of nuclear" in Japan, that is, a sum of "radiation" and "nuclear energy" was 132 b$, and the ratio between radiation and nuclear energy was 54 % : 46 %. Economic scale of utilization of radiation in Japan was 71 b$ (1 $=121 ¥) at a fiscal year of 1997[1-4]. The value of 71 b$ consisted of 60 b$ for industrial applications, 1 b$ for agricultural uses and 10 b$ for medical/health uses, respectively. Under the FNCA, 7 projects including the radiation application in the field of agriculture and medical/health have been implemented but the project in the field of industry is not including, even though the economic scale is much bigger than the other two fields. Under these backgrounds, a new project on application of electron accelerator was established.

The penetration of low energy electron beam is limited but it can be applied in various fields with development of irradiation system for products of liquid, solid and gas.

<u>Liquid:</u>

Radiation vulcanization of natural rubber latex

Degradation of polysaccharides for plant growth promotion

Waste water treatment

<u>Solid:</u>

Surface irradiation for sterilization/pasteurization of spices, seeds, etc.

Curing and crosslinking of films

<u>Gas:</u>

Flue gas treatment

Degradation of dioxins

2. Utilization of polysaccharides by radiation processing

Irradiation using gamma-ray from ^{60}Co and electron beam (EB) is widely used for bio-resources sterilization and modification of materials through degradation and crosslinking. For the modification of natural polymers using radiation, we found the induction of various biological activities for plants on degraded polysaccharides[5] and the method to produce the hydrogel using pure natural polymers such as carboxymethylcellulose (CMC), CM-starch and CM-chitin/chitosan through the crosslinking under certain radiation condition[6].

2.1. Degradation of polysaccharides and induction of biological activities

Polysaccharides such as chitosan[7] and alginate[5] can be degraded by irradiation. Radiation causes the cleavage of glycosidic link of polysaccharides, producing lower fractions. These degraded polysaccharides induced various kinds of biological activities[8], i. g., anti-microbial activity, promotion of plant growth, suppression of heavy metal stress, phytoalexins induction (Fig. 1).

Antibacterial activity: Irradiated chitosan at 100kGy in dry state was effective in increasing the activity and inhibited the growth of *E. coli* completely with the concentration of 3 μg/ml[9] (Fig. 2). The giant cells of *E. coli* observed by the treatment of irradiated chitosan suggested that the irradiated chitosan attached on the cell surface and inhibited the cell division.

Suppression of environmental stress: Effect of chitosan irradiated at wide range of irradiation doses on plants was examined. The stress with heavy metals such as vanadium (V) was relatively reduced by application of radiation-degraded chitosan. The recovery of growth and reduction of V levels in seedlings were obtained by the treatments with 100 and 200 μg/ml chitosan irradiated at 100 kGy in 1 % solution[10]. Lignocellulosic materials extracted from oil palm fiber, sugar cane bagasse and sawdust of *fagus* show the strong activity to suppress the heavy metal and salt stress on plants. The growth of plants suffering salt stress was clearly improved with lignocellulosic extracts especially at 90 kGy irradiation.

Induction of phytoalexins: Chitosan irradiated at 1000 kGy in solid state induced the high activity of pisatin (a phytoalexin induced in pea)[8]. The results suggest that the radiation-degraded polysaccharides involved the signal transduction, defense responses against pathogens and synthesis of phytoalexins.

2.2. Plant growth promotion

We found that the radiation-degraded alginate induced the plant growth promotion under hydroponics cultivation condition[5]. For rice, degraded alginate from 4 % alginate solution irradiated at 100 kGy (MW ca. 7000) impacts remarkable effect on growth promotion. Chitosan with 80 % degree of deacetylation and molecular weight 1.5×10^5 irradiated at 100 kGy in 10 % solution shows the growth promotion effect for plant *in vitro*. Figure 3 shows that the significant increase on the biomass of carrot callus is observed at the doses of 50-200 kGy. Chitosan irradiated at 100 kGy shows the strongest effect on the growth promotion of callus biomass (37 %). The supplementation of irradiated chitosan into rooting medium also showed the strong effect on the increase of fresh biomass (32 % for carrot, 26 % for strawberry and 32.3 % for *L. latifolium*), shoot height (25 % for carrot, 23 % for strawberry and 9.2 % for *L. latifolium*) and root length (21 % for carrot, 19 % for strawberry and 104.6 % for *L. latifolium*). The optimum concentrations for strawberry and *L. latifolium* incubated on rooting medium are *ca.* 50 mg/l and 40 mg/l, respectively. The survival ratio of transferred *L. latifolium* plantlets treated with irradiated chitosan was improved from 7.5 – 13 % after acclimatizing for 30 days in the greenhouse.

3. Radiation crosslinking of polysaccharides

The development of biodegradable polymer is important because it is friendly for environment and converted to CO_2 and H_2O by bacterial degradation in the soil. Using the technique for radiation crosslinking of PCL, radiation crosslinking of carboxymethylcellulose (CMC) was tested with a degree of substitution (DS) from 0.7 to 2.2 (Fig. 4).

It was found that irradiation of CMC with a high DS (2.2) and a high concentration (50 – 60 %) in an aqueous solution was favorable for high crosslinking of CMC (FEI et al, 2000). It is assumed that high radiation crosslinking of CMC was induced by the increased mobility of its molecules in water and by the formation of CMC radicals from the abstraction of H atoms of macromolecules in the intermediate products of water radiolysis. Carboxymethyl-starch (CMS) and CM-chitin/chitosan were also effectively crosslinked by radiation in 50 % solution. These crosslinked CMC, CMS and CM- chitin/chitosan hydrogel were easily digested in soil. These results show that some carbohydrate derivatives, CMC, CMS and CM-chitin/chitosan can be crosslinked under certain radiation condition and produced the biodegradable hydrogel for medical and agricultural use.

4. Irradiation system of liquid samples using low energy EB

4.1. Degradation of natural polymers

The low energy EB machine (250 keV, 10 mA) installed at JAERI-Takasaki is used for study radiation degradation of polysaccharides. The length and width of the beam window are 20 cm and 6 cm, respectively. The liquid irradiation vessel under EB is the cylindrical stainless steel with 25 cm diameter and 30.3 cm height. The vessel is equipped with magnetic stirrer at the bottom. Alginate concentration of 5 g/100 ml is prepared and

14 litters of alginate solution are used in the reaction vessel for EB irradiation. During irradiation the stirring speed is kept constantly at 20 rpm. Results of the viscosity decrease of alginate solution with various irradiation time and beam current are shown in Fig. 5.

The results indicated that the irradiation times required to decrease viscosity of alginate solution from ca. 1,200 cP to ca. 10 cP at different beam currents of 2.5, 5 and 10 mA are 90, 45 and 30 min, respectively. The viscosity is equivalent at the dose of 30 kGy of gamma-rays. Based on the results obtained for alginate, the low energy EB irradiation system seems to be a useful facility for radiation degradation of polysaccharides in solution and especially for large-scale application.

4.2. Radiation vulcanization of natural rubber latex (RVNRL)

Radiation-induced crosslinking of natural rubber in latex can be accomplished by irradiation natural rubber latex. Radioactive isotope ^{60}Co is used as a radiation source for R&D of RVNRL. However, the installation of ^{60}Co irradiation facility in natural rubber in latex dipping factory may not feasible due to high initial investment, high irradiation cost and decay of activity of 12 % per year. Development of a low-cost irradiator for natural rubber latex dipping factory is an urgent subject for further promotion of RVNRL technology. The low energy electron accelerator has fewer difficulties compared with ^{60}Co, and low investment and irradiation cost can be expected. The low energy electron accelerator has been proved to be a versatile, practical and economic radiation source for radiation processing such as crosslinking of plastic films and surface curing. However, the penetration of the low energy EB in natural rubber latex is limited. The problem of low penetration of the low energy EB was solved by means of an irradiation vessel with effective stirrer (Fig. 6).

5. Enhancement of plant growth by low energy EB

The average soybean yield is low (1.7 ton/ha) and unstable especially in small-scale soybean field. However, it is reported that 3 - 6 ton/ha seed yield can be obtained in well managed cultivation. We have investigating the effect of low energy EB irradiation on soybean seeds to enhance the yields. Seeds of soybean were irradiated in the dose range of 2 to 20 kGy using EB with different energy from 150 to 250 keV. Surface radiation of seeds enhanced the germination ratio. Growth promotion was also observed for irradiated seeds at the dose up to 10 kGy (Fig 7). Especially, significant promotion of root growth was observed on irradiated soybean. The number of rhizobia on the root of soybean irradiated at 20 kGy with 200 keV EB was increased ten times higher than that of unirradiated seeds. These results suggest that the irradiation of soybean seeds by low energy EB (surface irradiation) is effective to enhance the number of rhizobia on the roots and promote the growth.

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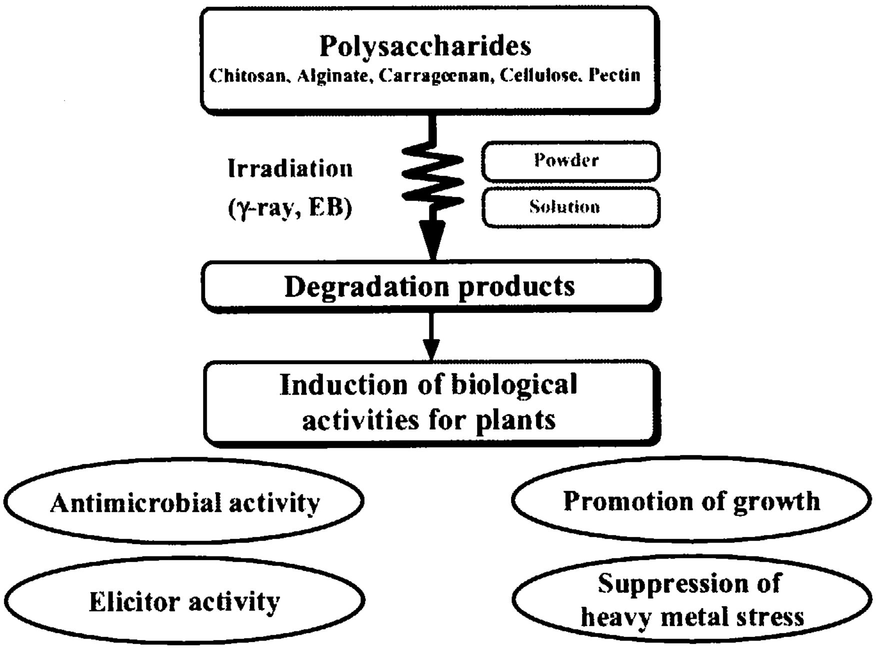

Fig. 1. Induction of biological activities on radiation-degraded polysaccharides

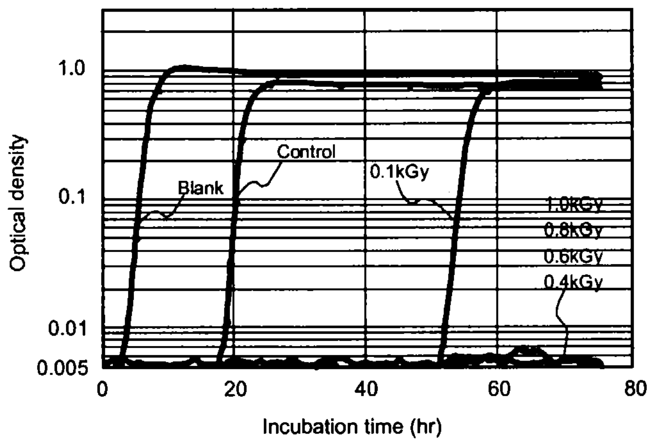

Fig. 2. Anti-bacterial activity of chitosan irradiated in 1% solution under O_2

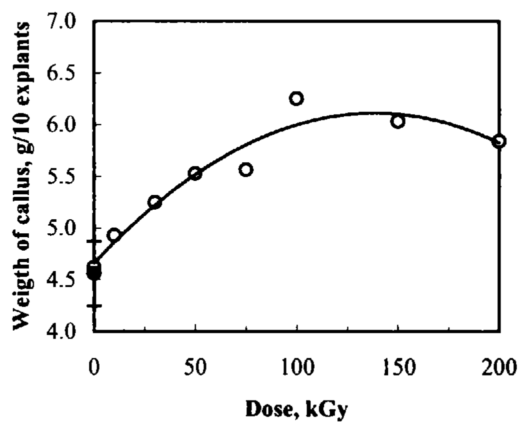

Fig. 3. Growth promotion of carrot callus by irradiated chitosan

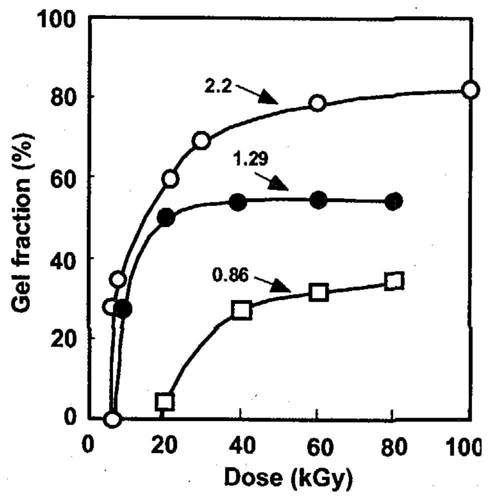

Fig. 4. Effect of substitution degree on radiation crosslinking of CMC

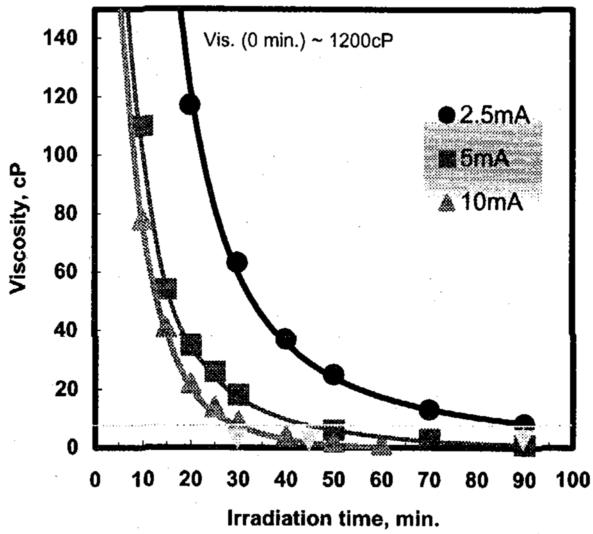

Fig. 5. Decrease in viscosity of alginate irradiated in solution by low energy EB

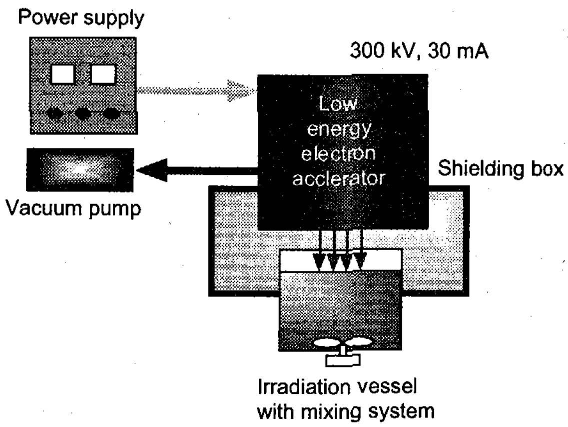

Fig. 6. Irradiation system for natural rubber latex using low energy EB

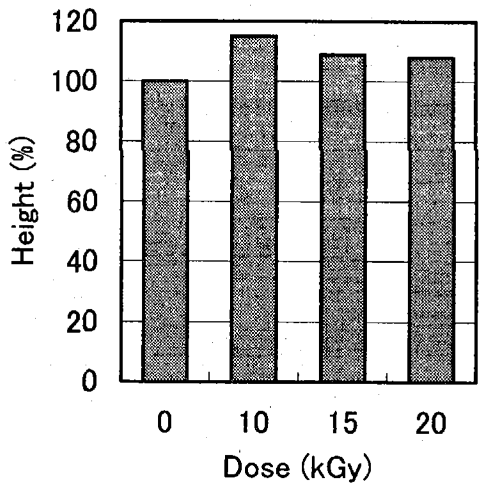

Fig. 7. Enhancement of soybean growth by surface irradiation with low energy EB