RADIATION DEGRADATION OF MARINE POLYSACCHARIDES BY LOW ENERGY ELECTRON BEAM

Country Report: JAPAN

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1. Introduction

Low molecular weight polysaccharides and/or oligosaccharides can be produced by degradation of corresponding polysaccharides including marine polysaccharides such as alginate, chitin/chitosan and carrageenan. Chemical, enzymatic and radiation processing technologies can be applied for degradation process.

Oligosaccharides have various novel biological effects such as plant growth promotion, anti-microbial activity, activation of immune system (activation of macrophages, stimulation of cytokine production, induce of phytoalexin), etc. [1-4]. Recently much attention has been paid to the application of radiation processing technology for degradation of natural polysaccharides due to several reasons, for instance:

- Carrying out at room temperature
- Ease of process control and large scale application
- Economic competitiveness to alternatives

Both gamma Co-60 and electron beam can be applied for degradation process [5,6]. Recently an unique design of low energy electron beam machine can be considered as a feasible economical facility for the purpose of liquid irradiation [6].

In this communication, the recent research results of radiation degradation of marine polysaccharides namely alginate, chitosan and carrageenan are presented.

2. Low Energy Electron Beam (LEEB) machine

The LEEB machine (250keV, 10mA) installed recently at Takasaki Radiation Chemistry Research Establishment is used for study. The length and width of the beam window are 20cm and 6cm, respectively. The liquid irradiation vessel under EB is cylindrical stainless steel with 25cm diameter and 30.3cm height. The vessel is equipped with magnetic stirrer at the bottom. More details are described in the presentation of Dr K. Makuuchi in this workshop.

3. Radiation degradation of marine polysaccharides

3.1. Alginates

Alginates composed of three types of block polymers namely polyglucuronate (poly G), polymannuronate (poly M) and copolymer (poly G-M) distributed in random sequences. Alginates have widespread applications in the food and drink, pharmaceutical, bioengineering and textile printing industries. Worldwide annual production is about 30,000 tons [7]. Recently, a plant growth promoter product named 'T&D' made from radiation degraded alginate in solution by gamma Co-60 has been commercialized [8].

In this experiment, alginate concentration of 5g/100ml is prepared and an amount of alginate solution of 14 litters is used in the reaction vessel for EB irradiation. During irradiation stirring speed is kept constant at 20rpm. Viscosity of alginate solution samples is measured in 25^{o}C by rotary viscometer (TV-20 Tokimec Co. Ltd. Japan) and molecular weight of irradiated alginate is measured by GPC instrument equipped with three TSK gel PW_{XL} columns (300x 7.8 mm) in series (G6000 PW_{XL}, G3000 PW_{XL} and G2500 PW_{XL}; Tosoh Co. Ltd., Japan).

Results of the viscosity decrease of alginate solution with various irradiation time and beam current are shown in Fig.1. The results indicated that the irradiation times required to decrease viscosity of alginate solution from about 1,200 to about 10cP at different beam currents particularly 2.5, 5 and 10mA are 90, 45 and 30min., respectively. In comparison with gamma Co-60 irradiation regarding to viscosity (see Fig. 2), the dose of about 30kGy is needed.

Table 1. The molecular weight and molecular weight distribution of alginate irradiated by gamma Co-60 and LEEB.

MW	Alginate powder (0kGy)	Gamma Co-60 (10kGy/h), 40kGy	LEEB (10mA), 35min.
Mw	136,695	8,898	12,667
Mn	50,702	7,410	7,837
Mw/Mn	2.70	1.20	1.62

Regarding to molecular weight distribution, Mw/Mn of oligoalginate is narrower than that of alginate.

Based on the results obtained for alginate, it can be said that LEEB machine is an effective tool for degradation of alginate in solution.

3.2. Chitosan

Chitosan is the N-deacetylated derivative of chitin, a naturally abundant mucopolysaccharide, homopolymer of β-(1$\rightarrow$ 4)-linked N-acteyl-D-glucosamine. Chitosan has a wide range of application fields, such as in waste water treatment, in medicine and cosmetics, in food preservation and functional food, etc. The production of chitosan is currently based on crab and shrimp shells discarded as a food industry waste. The global annual estimate of shellfish processing discards is around $5x10^6$ metric tons [9]. Thus, disposal of shellfish processing wastes has been a challenge for most of the shellfish-processing countries. Therefore, production of value-added products such as chitin/chitosan, oligomers and their derivatives for utilization in different fields is of utmost interest. Recently two products made from radiation degraded chitosan named OLICIDE in Vietnam and OSAN in Thailand used as plant protector and plant-growth promoter have been commercialized.

In this experiment, chitosan (DA~85%) is dissolved in 2% acetic acid with concentration of 5g/100ml. Irradiation of chitosan solution by LEEB is carried out as above described for alginate solution.

Results of the viscosity change with irradiation time are shown in Fig.3. The viscosity of chitosan solution decreases from 820cP to about 8cP after 30 min. irradiation. The irradiation time of 30 minutes by LEEB is equivalent of 20kGy with gamma Co-60 (10kGy/h).

3.3. Carrageenan

Carrageenans are composed of high sulfated alternating alpha (1-3) and beta(1-4) linked galactose residues. There are three types of carrageenans namely *kappa*, *iota* and *lambda*. All types have similar D-galactose backbones but they differ in degree of sulfation, extent of branching, solubility and ability to form gels. Carrageenan exist naturally in states of very high degree of polymerization. Carrageenan has a broad range of applications. They are used principally as stabilizer, thickeners, emulsifiers and gelling agents in foods. In addition to food additives, carrageenan has been used in cosmetics, pharmaceutical, pesticides, and biotechnology. Worldwide annual production is 40,000 tons with 43% production share from Philippines [10].

Due to highly viscous of carrageenan solution, the concentration of 1g/100ml is prepared in this study. Irradiation of carrageenan solution by LEEB is carried out as above described for alginate and chitosan solution.

The change of viscosity with irradiation time is shown in Fig. 4. It can be observed that the viscosity of 1% carrageenan solution decreases sharply in short time by LEEB irradiation. This is probably due to low concentration of polysaccharide particularly carrageenan. In comparison with gamma Co-60 irradiation regarding to viscosity result, 15 min. LEEB irradiation at beam current of 5mA is equal to 5 kGy irradiated by gamma Co-60 radiation with dose rate 1kGy/h.

4. Conclusions

- Viscosity of alginate, chitosan and carrageenan solution decreases markedly with the increase of LEEB irradiation time and beam current. Furthermore, the viscosity is reduced sharply in short time for polysaccharide solution with low concentration, for instance carrageenan solution of 1 %.
- For radiation degradation of marine polysaccharides, it is recommended that low molecular weight type of starting polysaccharides should be used.
- Low energy electron beam machine seems to be a useful facility for radiation degradation of polysaccharides in solution and especially for large scale application.

References

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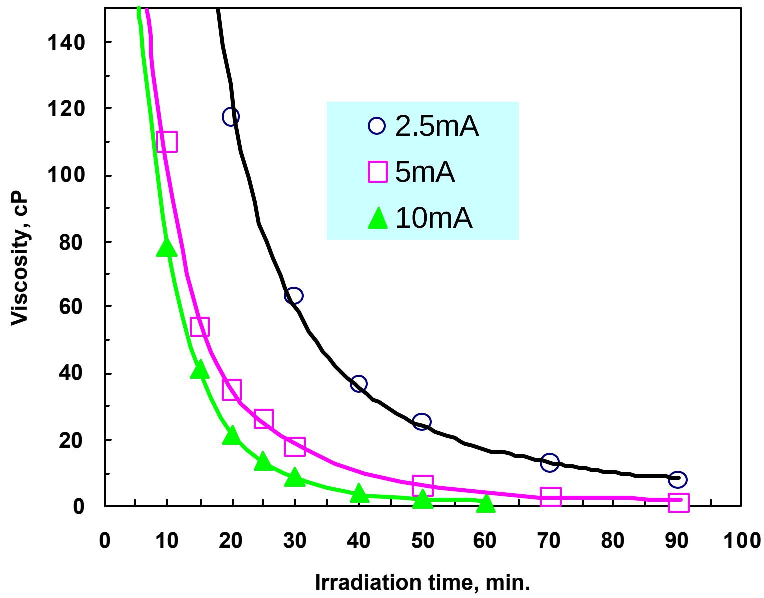

Fig. 1. Effect of irradiation time & beam current on viscosity of alginate solution (5g/dL)

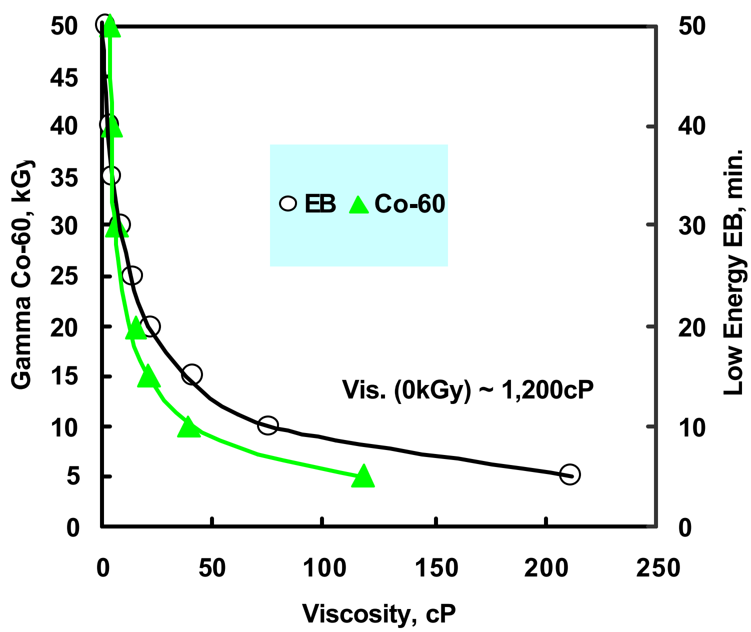

Fig. 2. The decrease of the viscosity of alginate solution (5g/dL) irradiated by gamma Co-60 (10kGy/h) and low energy EB (250keV, 10mA)

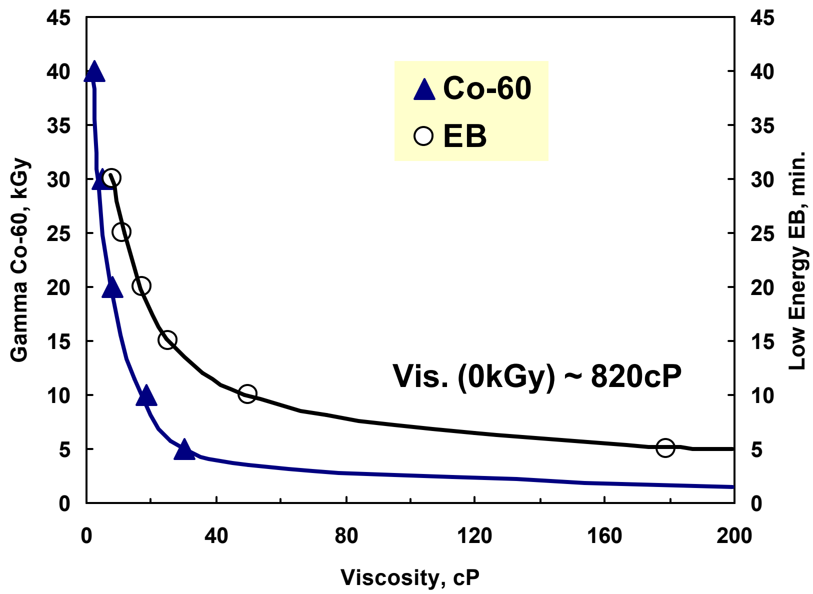

Fig. 3. The decrease of the viscosity of chitosan solution (5g/dL, 2% CH_3COOH) irradiated by gamma Co-60 (10kGy/h) and low energy EB (250keV, 10mA)

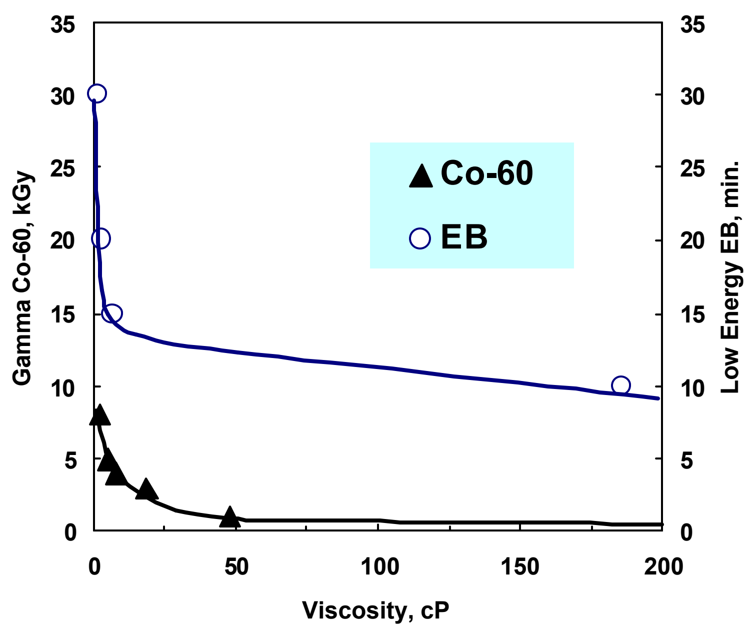

Fig. 4. The decrease of the viscosity of carageenan solution (1g/dL) irradiated by gamma Co-60 (2kGy/h) and low energy Electron Beam (EB - 250keV, 5mA)