

DEGRADATION OF SODIUM ALGINATE BY LOW ENERGY ELECTRON BEAM

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ABSTRACT

DEGRADATION OF SODIUM ALGINATE BY LOW ENERGY ELECTRON BEAM. High viscosity (HV) and low viscosity (LV) alginate prepared in 5% solutions were irradiated by low energy electron beam (LEEB) at 55°C and ambient temperature respectively. Oligoalginates with molecular weight lower than 20,000 Da and broad molecular weight distribution were obtained until 60 minutes of irradiation. The decrease in molecular weight was accompanied by appearance of UV absorbance peak at 265 nm. LV alginate was preferable to use as raw material for LEEB irradiation process than HV alginate.

Key words : Sodium alginate, degradation, radiation, low energy electron beam

ABSTRAK

DEGRADASI NATRIUM ALGINAT DENGAN MENGGUNAKAN MESIN BERKAS ELEKTRON ENERGI RENDAH. Alginat viskositas tinggi (HV) dan rendah (LV) dengan konsentrasi 5% diirradiasi dengan menggunakan mesin berkas elektron energi rendah (MBE - Energi Rendah) masing-masing pada suhu 55 °C dan suhu ruang. Setelah diirradiasi selama 60 menit diperoleh oligoalginat dengan berat molekul lebih kecil dari 20.000 Da dan memiliki distribusi berat molekul yang lebar. Penurunan berat molekul disertai dengan penampakan puncak absorpsi UV pada 265 nm. Alginat viskositas rendah lebih baik digunakan sebagai bahan baku pada proses iradiasi dengan menggunakan MBE - Energi Rendah dibandingkan dengan alginat viskositas tinggi.

Kata kunci : Natrium alginat, degradasi, radiasi, mesin berkas elektron energi rendah

INTRODUCTION

Alginate belongs to the family of linear polysaccharides composed of 1-4-linked β -D-mannuronic acid (M) and its C-5-epimer α -L-guluronic acid (G)[1]. Alginates have been used in wide range of commercial products as food, drinks, and pharmaceuticals and in textile industry as stabilizer, viscosifier and gelling agent[2]. Recently oligomers of alginate (oligoalginate) can be used for growth- promoter of the bifidobacteria and plant [3-5]. Additionally, same oligomers enhance plant germination and shoot elongation[6]

It has been reported that sodium alginate can be degraded by acid hydrolysis[7] or enzymatic [8]. On the other hand, radiation provides a more convenient technique for polysaccharides degradation [9]. Although degradation of sodium alginate by gamma-rays techniques has already been studied [10-12], sodium alginate degradation by low energy electron beam (LEEB) has not yet been investigated.

LEEB is a convenient radiation machine which has an advantage with respect to economy, safety, operational simplicity and versatility. In addition, comparing with high energy electron beam and gamma-

rays, a self-shielded LEEB system needs much lower initial investment. The disadvantage of LEEB is its limited penetration, but applications in various fields has already been reported [13]. The purpose of this research work is to study the degradation of sodium alginate irradiated by LEEB and evaluate with respect to viscosity, molecular weight, molecular weight distribution and color changes.

EXPERIMENTAL METHOD

Materials

In the experimental work, sodium alginate powder (Kimitsu ALGIN B5) was purchased from Kimitsu Chemical Industries Co. Ltd., Japan. Viscosity of ALGIN B5 solution (1% aq.) at 20°C is 550 cP. The ALGIN was irradiated to 25 kGy with gamma rays (10kGy/h) to reduce its solution viscosity. Viscosity of irradiated ALGIN solution (1% aq.) at 25°C reduced to 15 cP. The raw material is called high viscosity alginate (HV). Gamma-rays pre irradiated called low viscosity

alginate (LV). This material was used without further purification. Other used chemicals were at technical grade of purity.

Irradiation

In this study, sodium alginate solution was irradiated with a 250 keV-10 mA electron accelerator using a vessel type irradiator. The irradiator was made of stainless steel and equipped with stirrer placed on the bottom of the vessel with the purpose to facilitate homogeneous degradation. The amount of 14 liter of 5% HV solution was put into the reaction vessel and irradiated at elevated temperature (55 °C). LV was irradiated at ambient temperature with various beam current (mA) and irradiation time. The solution was stirred throughout irradiation.

Analytical Procedures

The viscosity of alginate solutions was determined at 25 °C by rotary viscometer (TV-20 Tokimec Co Ltd., Japan).

Irradiated samples were analyzed by Gel Permeation Chromatography (GPC) for this purpose HLC-8020 (Tosoh Co. Ltd., Japan) instrument equipped with three TSK gel PW_{XL} columns (300 × 7.8 mm) in series (G6000 PW_{XL}, G3000 PW_{XL} and G2500 PW_{XL}; Tosoh Co. Ltd., Japan) was used in combination with a TSK guard column PW_{XL} (40 × 6.0 mm). The flow rate of 0.1 M sodium nitrate aqueous solution was 0.5 ml/min at the temperature of 40 °C. The eluent was monitored by RI-8020 differential refractometer at 40°C. Molecular weights were determined by use of calibration curve for 0.1% (w/v) standards pullulan, poly (ethylene oxide) and poly (ethylene glycol).

UV-visible spectroscopy of irradiated alginate solution was performed at 25 °C using a Shimadzu spectrophotometer UV-265FW in the range of 200-400 nm to determine the absorbance. The aqueous solution consisting of 0.025 % (w/v) of polymer was analyzed.

RESULT AND DISCUSSION

Change in Viscosity and Molecular Weight of Alginate Solution After LEEB Irradiation.

Alginate solutions with different viscosities and weight average molecular weight (Mw) were obtained after irradiation. 5% HV alginate solution required heating during irradiation due to its very high viscosity. In the case of low viscosity alginate solution (LV), the sample was irradiated without heating. In Figure 1 the viscosities of irradiated alginate solution of HV and LV are compared. There was gradual decrease in the viscosity of LV alginate solution. Even after

20 minutes of irradiation, the viscosity of HV was still over 5,000 cP, whereas that of LV reached around 20 cP. After about 40 minutes of irradiation, the viscosities of these alginate solutions reached saturation with a value lower than 5 cP. The initial viscosities of HV and LV alginate were over 5,000 cP and around 1,200 cP, respectively. It can be explained that sharp decrease in viscosities occurred in the first 40 minutes irradiation. The delayed reduction of HV alginate compared to LV alginate can be attributed to the in homogeneity of irradiation due to the higher viscosity of HV alginate.

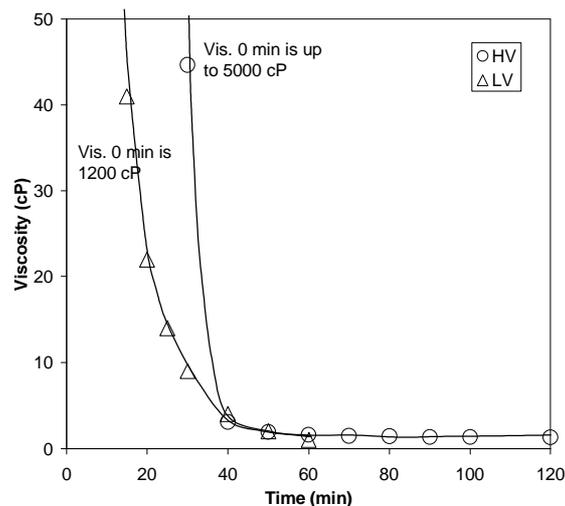


Figure 1. The decreased of viscosity of HV and LV alginate solution irradiated by LEEB (250 keV ; 10 mA)

The initial Mw of HV and LV alginates solutions were ca. 1,100,000 Da and 300,000 Da respectively. Figure 2 presents average molecular weight (Mw) of irradiated alginate solutions. As seen from the figure, abrupt change in molecular weight was noted both for HV and LV alginate solutions. After irradiation for 40 minutes at 10 mA, the viscosities of HV and LV were almost the same but with different corresponding Mw.

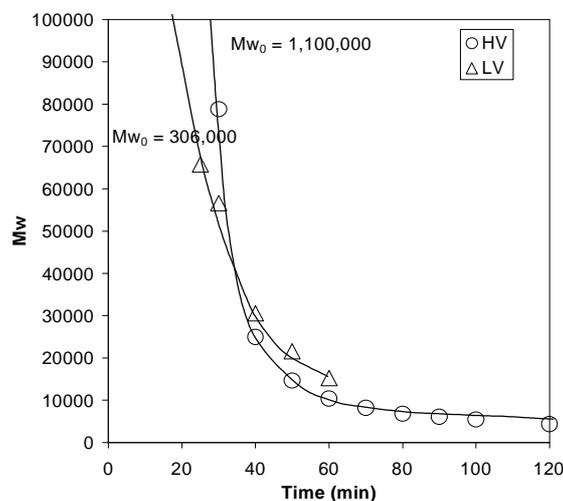


Figure 2. The decreased of molecular weight (Mw) of HV and LV alginate solution irradiated by LEEB (250 kV).

The Mw of HV alginate solution was lower compared to that of LV alginate solution. This was probably due to heating at 55 °C not only facilitated mixing process in the beginning of irradiation, but also enhanced the degradation process through thermal effect.

The viscosities of irradiated LV alginate solution by various beam currents are shown in Figure 3. The viscosity of 5% alginate solution decreased remarkably at the initial stage and then gradually leveled off with time and beam current increase. The viscosity decreased remarkably after 10 minutes of irradiation with beam current of 5 and 10 mA, whereas 20 minutes for 2.5 mA were needed to level of this parameter. The viscosities of the alginate solutions were measured for the samples irradiated by 2.5 mA beam for 90 minutes; 5 mA for 50 minutes and 10 mA for 35 minutes. Their viscosities decreased from 1,200 cP. to below than 10 cP.

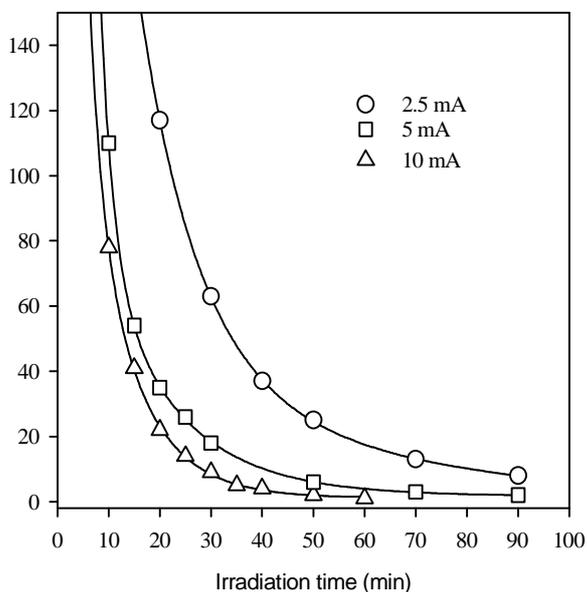


Figure 3. Effect of irradiation time and beam current on viscosity of LV alginate solution (5 g/100 mL) irradiated by LEEB (250 keV).

GPC elution curves of control (raw material) and LV irradiated by LEEB with current of 10 mA for 0, 10, 30 and 60 min are presented in Figure 4. The peak of the elution shifted toward in the case of longer irradiation (sample), indicating chain scission of alginate. The same phenomena for alginate irradiated by 2.5 and 5 mA have been observed.

Figure 5 shows the decrease of Mw of irradiated LV alginate by different beam current. Molecular weight decreased remarkably after 10 minutes by 2.5 and 5 mA beam current, whereas lesser time was for the abrupt change in Mw at 10 mA. Then, decrease became lower if irradiation time increased. The Mw of sample irradiated at 2.5 mA for 90 minutes; 5 mA for 70 minutes and 10 mA for 35 minutes were lower than 20,000 Da.

As expected, the viscosity and molecular weight of alginate decreased significantly after irradiation.

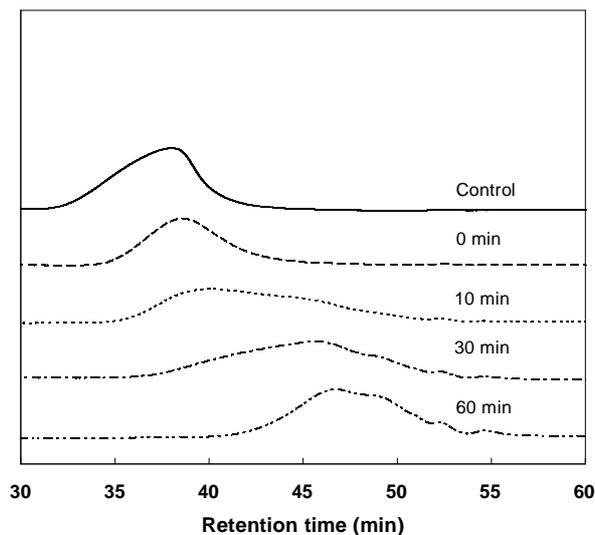


Figure 4. GPC elution curves of alginates irradiated to 0, 10, 30 and 60 minutes in aqueous solution.

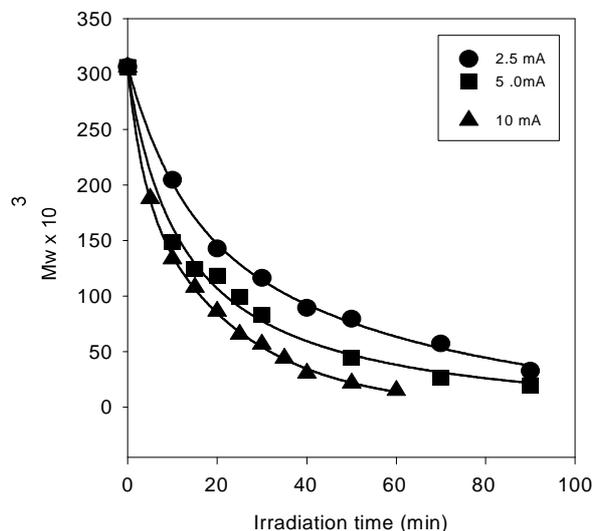


Figure 5. Effect of irradiation time and beam current on decreasing of Mw of LV alginate solution (5 g/100 mL) irradiated by LEEB (250 keV).

Similar results were also obtained for other irradiated polysaccharides such as carrageenan [14], citrus pectin [15], agar [16] and chitosan [17]. Alginate has glycosidic linkage similar with others polysaccharides mentioned above. These polymers are typical condensation polymers degradable through random degradation process. In random degradation, molecular weight drop rapidly at the beginning and then remains constant [18]. In some polymers, radiation induced random degradation and supposed that there is little or no monomer is produced even after extensive main chain fracture. Each monomer unit is equally liable to fracture after absorbs energy. The reported that there is no big difference in the depolymerization of chitosan for irradiation dose of 100 and 200 kGy¹⁷. As it was established previously, irradiation induced scission of 1-4 glycosidic bonds of polysaccharides. In this

experimental work, it is evident that LEEB irradiation induced degradation of alginate through chain scission by random degradation process. The degradation process is fast by using 10 mA of beam current.

The molecular weight distribution for HV and LV irradiated alginates are shown in Figure 6.

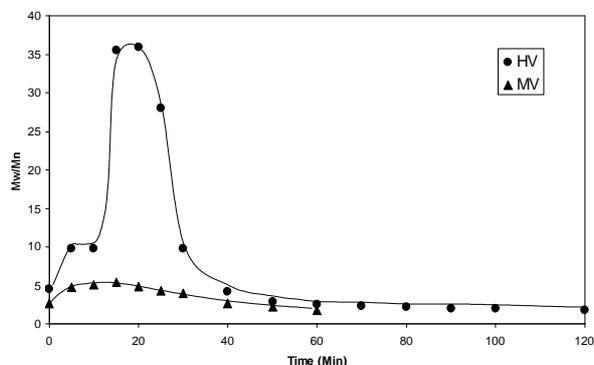


Figure 6. The molecular weight distribution of HV and LV alginate solutions (5g/100 mL) irradiated by LEEB (250 kV).

At the initial stage of irradiation, the molecular weight distributions of alginate are broad suggesting time dependent degradation. The narrow distribution was reached after 40 minutes of irradiation. It can be explained that at initial stage, alginate was degraded only on the surface. Some part of alginate still unirradiated because the solution was still viscous. With increase in irradiation time, more alginate degraded due to lower viscosity of the solution and after the time mentioned above, whole volume of solution was degraded homogeneously.

Color Change of Alginate Irradiated By LEEB

The color change was evaluated on the base of UV absorbance. Figure 7 shows the photographs of alginate solution samples irradiated by 10 mA beam for 5 and 60 minutes. The color became more intense brown in the case of samples irradiated for 60 minutes. Figure 8 shows the UV spectra of alginates irradiated for 40 and 60 minutes: a new absorption band at 265 nm was observed. The intensity of the peak increased for longer irradiation time. Figure 9 shows the difference of optical density of HV and LV of alginate solution irradiated by LEEB (250 keV; 10 mA). The OD of irradiated HV is higher than that of irradiated LV. The same result was also observed in the case of HV irradiated by gamma rays at elevated temperature.

Nagasawa et al (2000) observed a new absorption band at 265 nm for alginate irradiated by gamma rays and proposed that color change occurred due to double bond formation by chain scission [12]. As it is already known, irradiation changes the chemical structure of material. It can be explained that in the case of alginate solution irradiated

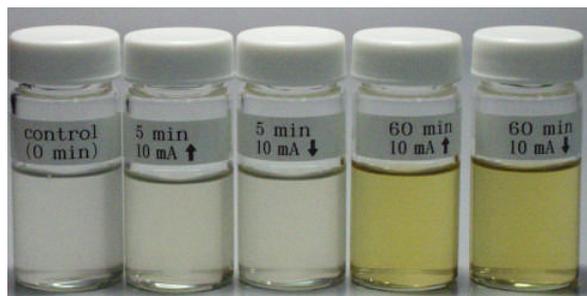


Figure 7. Color change of alginate solution irradiated using LEEB (250 keV; 10 mA) (↑ = upper level of the vessel ↓ = bottom level of the vessel).

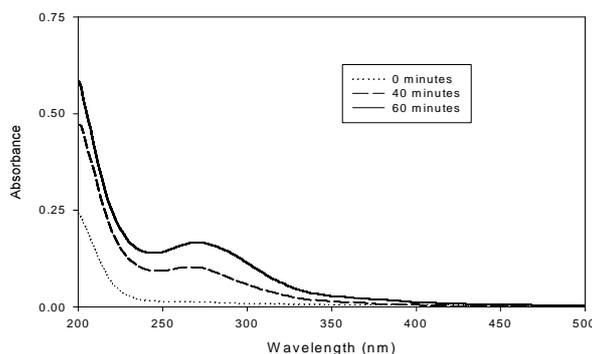


Figure 8. UV spectrum of alginate solution irradiated 0, 40 and 60 minutes using LEEB.

by LEEB, the decrease in molecular weight is accompanied by changes of the chemical structure which resulted changes of color. The color of irradiated HV was more intense than that of irradiated LV probably because of thermal effect of 55 °C during irradiation of HV.

Conversion of Irradiation Time of LEEB With Irradiation Dose of LEEB

As it was mentioned before, irradiation using LEEB is supposed to be more feasible and economic than those with a Co-60 or with a medium and high energy electron accelerator. However LEEB has disadvantages such as low penetration, high absorption and wide scattering in air. According to Makuuchi, K. (to be published) [20], energy lost from the window during irradiation by LEEB is around 30%. Then, with 12.5 cm thickness of air; only 40% of the energy remains was absorbed by samples. Estimation of the dose absorbed in irradiated samples was based on the equation:

$$1 \text{ kGy} = 1 \text{ kJ/kg} = 1 \text{ kW/s/kg} = (1 \text{ keV} \times A) \text{ s/kg}$$

The energy consumed for 60 minutes irradiation by LEEB (250 keV; 10 mA) is:

$$250 \text{ keV} \times (10 \times 10^{-3} \text{ A}) \times (60 \text{ min} \times 60 \text{ sec/min}) = (9 \times 10^3) \text{ kW s}$$

In this experiment, 14 L of LV alginate solution sample related to 15 kg.

The absorbed dose by 15 kg of LV alginate solution is:

$$0.4 \times 0.7 \times (9 \times 10^3) \text{ kWs} / 15 \text{ kg} = 168 \text{ kGy}$$

The irradiation time of LEEB (250 keV; 10 mA) with 15 kg alginate solution was converted to dose (kGy). The estimation dose presents on Table 1.

Table 1. The estimated value of dose absorbed of 15 kg alginate solution irradiated by LEEB (250 keV;10 mA).

Times (minutes)	Times (second)	Dose (kGy)
0	0	0
5	300	14
10	600	28
15	900	42
20	1200	56
25	1500	70
30	1800	84
35	2400	112
40	3000	140
50	3600	168
60	4200	196

CONCLUSION

Oligoalginates with molecular weight lower than 20,000 Da. and broad molecular weight distribution were obtained by LEEB irradiation. The decrease in molecular weight was accompanied by appearance of UV absorbance peak at 265 nm. LV alginate was preferable to use as raw material in LEEB irradiation process than HV alginate. Degradation of sodium alginate by LEEB induces time dependent degradation.

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