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Radiation degradation studies of carrageenans

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ABSTRACT

The radiation degradation yield (G_d) of kappa, iota and lambda carrageenans was compared in solid and in 1% aqueous solution in air at ambient temperature. G_ds obtained in solid and aqueous form did not vary with the different types of carrageenan.

The chemical structural changes of carrageenans were accompanied by appearance of UV absorbance peak at 260 nm and a characteristic FT-IR band at 1728 cm^{-1}. Changes in the FT-IR finger print regions were observed at high doses of the aqueous solution.

Radiation-induced desulfation increased the acidity of the carrageenans. The number of reducing end groups increased with dose with greater susceptibility in κ-carrageenan.

1. Introduction

Carrageenan belongs to the family of polysaccharides, extracted from many species of red algae, the Rhodophyceae. They are mixtures of water-soluble, linear, sulfated galactans. The main types of carrageenan are kappa (κ-), iota (ι-) and lambda (λ-). These different types are classified according to the number and position of sulfate groups. Kappa carrageenan is composed of alternating α(1,3)-D-galactose-4-sulfated and β(1-4)-3,6-anhydro-D-galactose. Iota carrageenan on the other hand is composed of alternating α(1,3)-D-galactose-4-sulfated and β(1-4)-3,6-anhydro-D-galactose-2-sulfate. Lambda carrageenan differs from kappa and iota carrageenan by having a disulfated-D-galactose residue and no 4-sulfate ester group but has varying amounts of 2-sulfate ester groups (Fig. 1).

Degradation of polysaccharides has recently drawn considerable interest due to their enormous applications especially in the field of medicine. The oligomers formed have found concrete uses in the acceleration of wound healing process, reduction of cholesterol level in blood, some anti-cancer and tumor activity. Oligomers from carrageenan have also been quite useful in the medical field. Oligo-kappa carrageenans induce secretion of laminarinase from Rubus cells and protoplast (Patier et al., 1995). Degraded λ-carrageenan is reported to have tumor inhibiting activities (Zhou, Sun, Xin, Zhang, & Xu, 2004; Zhou et al., 2005). Oligomers from carrageenans suggest promising antiherpetic, anti-HIV (human immunodeficiency virus) activities and as anti-infectants (Carlucci et al., 1997; Cáceres, Carlucci, Damonte, Matsuhiro, & Zúñiga, 2000; Katsuraya et al., 1994; Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 2000; Yamada et al., 1997).

Degradation of polysaccharides can easily be carried out either by chemical or enzymatic hydrolysis. Recently, degradation by radiation processing of polysaccharides has gained much attention due to its technological effectiveness in producing low molecular weight oligomers. Oligomers prepared from radiation degradation have found concrete application not only in the biomedical field but also in agriculture, as plant growth promoter (Hien et al., 2000; Kume, Nagasawa, & Yoshii, 2002). In recent years, development of new products from radiation processed/modified carrageenan has been a subject of research. Products such as PVP-carrageenan hydrogel, radiation dose indicator, and radiation processed carrageenan oligomers as plant growth promoter have been developed from carrageenan (De la Rosa, Abad, Relleve, & Aranilla, 2002). Carboxymethyl carrageenan has been synthesized and tested as metal adsorbent (Aranilla, 2008). The key to the successful development of materials from radiation processed carrageenan is the knowledge of the radiolytic products formed after degradation. Some related researches on this topic have already been published (Abad, Okabe, Koizumi, & Shibayama, 2006; Abad et al., 2004, 2008; Relleve et al., 2005). This paper would focus on the chemical and structural characterization of irradiated carrageenans (κ-, ι-, and λ-carrageenan) in solid and aqueous form.

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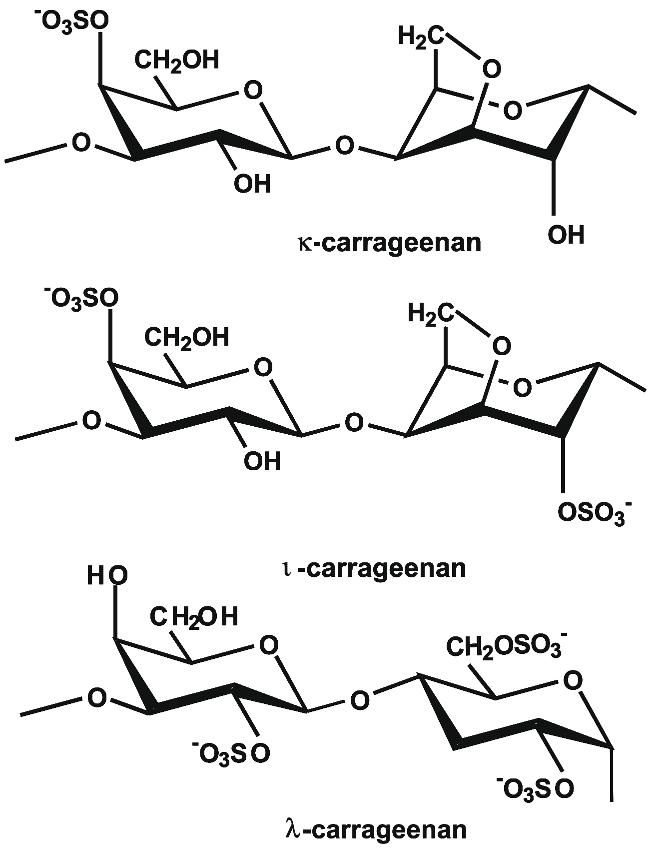

Fig. 1. Idealized structure of κ-, ι-, and λ-carrageenan.

2. Materials and methods

2.1. Materials

Refined κ-, ι-, and λ-carrageenan were obtained from Shemberg Corporation, Philippines. The carrageenans were dissolved in distilled water and precipitated with isopropyl alcohol. The precipitated carrageenans were dissolved in a buffer solution containing 0.1 M NaCl and 0.005 M ethylenediaminetetraacetic acid (EDTA). The samples were dialyzed (Mol. wt. cut-off = 12,000–14,000) against a NaH_2PO_4/Na_2HPO_4 buffer solution for 72 h. The dialyzed solutions were reprecipitated with isopropyl alcohol and freeze dried.

2.2. Irradiation of kappa carrageenan

Irradiation of the purified kappa carrageenan was carried out using the Co-60 facility of the Takasaki Radiation Chemistry Research Establishment at different conditions (powder and 1% aqueous solution in air and at ambient temperature). Samples were irradiated at a dose rate of 10 kGy/h (for 10–200 kGy) and 1 kGy/hr (for 0.5–6 kGy).

2.3. Molecular weight measurement

GPC analyses were performed on a Tosoh chromatograph equipped with DP-8020 pump, CO-8020 column oven, RI-8020 refractive index detector and four TSK gel PWXL columns in series (G6000 PWXL, G4000 PWXL, G3000 PWXL, and G2500 PWXL. Elution was carried out using 0.1 M $NaNO_3$ (to suppress electrostatic effects) as the mobile phase at a flow rate of 0.5 ml/min. The temperatures of the column and detector were both maintained at 40 °C. A calibration curve was constructed using polyethylene oxide as standards. All molecular masses reported in this work are based on PEO standards and are not absolute.

2.4. Spectral analyses

FT-IR spectra of samples in KBr pellets (1 mg/100 mg KBr) were measured using an FT-IR Nicolet Magna 550 at ambient temperature in the region of 4000–400 cm^{-1}.

UV–visible spectroscopy of carrageenan solutions was performed using a Shimadzu spectrophotometer UV-265 FW at ambient temperature and at 0.025% (w/v) concentration.

2.5. Chemical analyses

The reducing group of the carrageenans was determined using the Nelson–Somogyi method of analysis with galactose as the standard (Hodge & Hofreiter, 1962).

The total acidity of the carrageenans was determined by acid–base titration method. Carrageenan solutions were titrated against standardized NaOH using a phenolphthalein indicator to determine end point. The acidity was reported as % H_2SO_4 in carrageenan.

3. Results and discussion

3.1. Radiation degradation yield of carrageenans

Radiation degradation yield (*Gd*) is defined as radiation chemical yield which represents the number of radiolysis events caused by the absorption of 100 eV of radiation. G_d (mol/J) expresses the degradation susceptibility of the polymer during radiation and can be calculated according to the equation based on the theory of radiation degradation:

$$G_d = \frac{1}{D}\left(\frac{1}{Mn} - \frac{1}{Mn_0}\right) \quad (1)$$

where Mn is the number-average molecular weight at absorption dose; Mn_0 is the initial number-average molecular weight; *D* is the absorbed dose in kGy. GPC profiles of the different carrageenans show the typical curves of increasing retention time with increasing radiation dose due to degradation as demonstrated in Fig. 2A–C (ι-carrageenan only). Fig. 3-A1 and B1 shows the degradation of the different carrageenans with radiation dose in powder and aqueous form. Both show a steep decrease in weight average molecular weight (Mw) with dose for all types of carrageenan. Decrease in Mw starts to plateau at a dose of 50 kGy for the solid carrageenans while the plateau starts at a small dose of 2 kGy for 1% aqueous solution. This is expected in solutions due to the indirect effect of water radiolysis products (OH radical) on the polysaccharide. Previous paper also reported this same trend (Relleve et al., 2005). The reciprocals of Mw are shown in Fig. 3A2 and B2. The slope of each curve gives the G_d. As seen from the graph, very slight differences in G_d were observed for the different types of carrageenans both in solid and aqueous solution. The computed G_d of the carrageenans at different conditions is shown in Table 1. The G_ds in powder form were as follows: 2.5, 2.7, and 2.3×10^{-7} mol/J for κ-, ι-, and λ-, respectively. These values are slightly higher than what was previously reported ($G_d = 1–1.3 \times 10^{-7}$ mol/J) (Relleve et al., 2005) probably because the carrageenans used in this study were purified.

In aqueous solution, the concentration of the polymer has to be considered in the computation of the G_d since Eq. (1) is based on 1 kg polymer. Hence, the G_d in aqueous solution is as follows:

$$G_d = \frac{c}{D}\left(\frac{1}{Mn} - \frac{1}{Mn_0}\right) \quad (2)$$

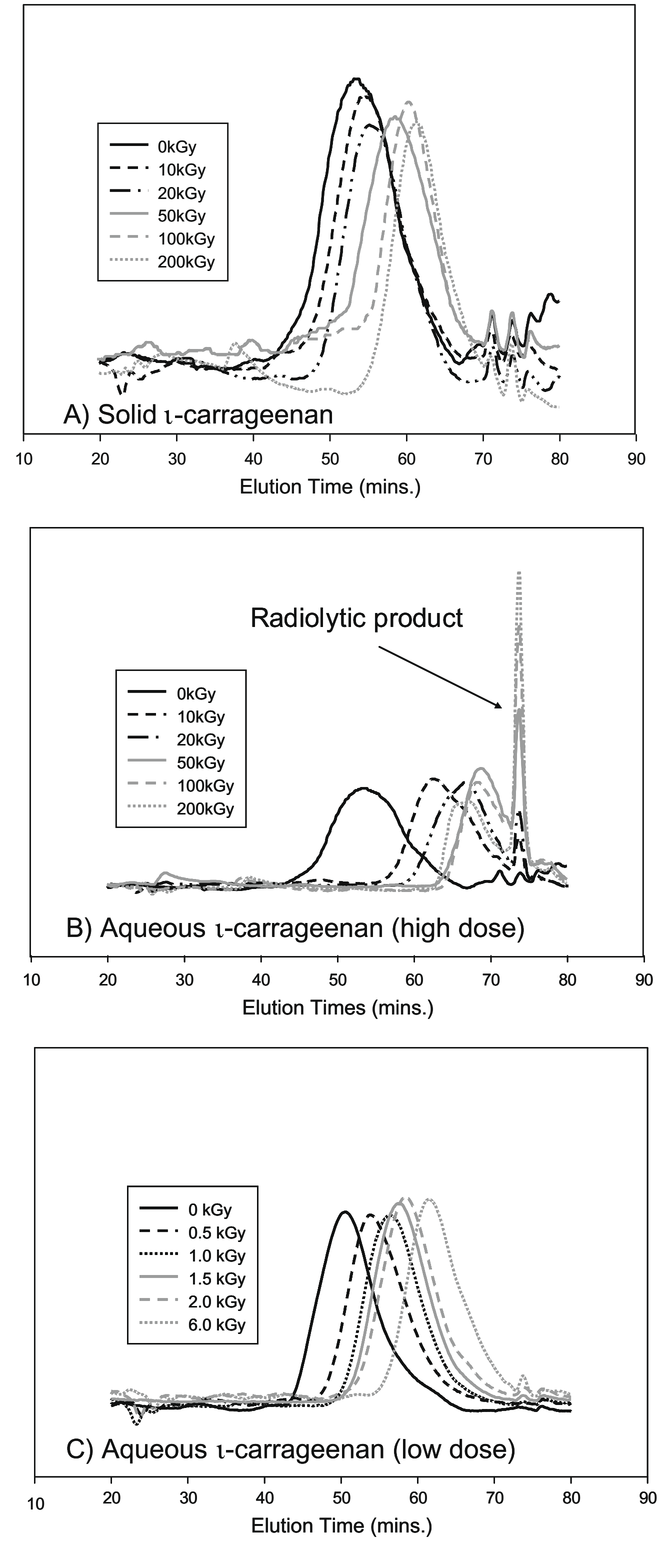

Fig. 2. GPC profile of ι-carrageenan irradiated in solid and in aqueous solution (1%) at different doses.

where *c* is the fractional weight of carrageenan solution (Ulanski & Von Sonntag, 2000).

Irradiation of 1% aqueous solution of carrageenan did not yield further decrease in Mw beyond 50 kGy as shown by the retention time which remained steady starting at this dose. Instead, increase in intensity of the radiolytic product peak (RT = 73.7 min) was seen at this dose and beyond (Fig. 2B). Approximately, the minimum DP obtained from the gamma irradiation of aqueous κ-, ι-, and λ-carrageenan at high doses were 7, 8, and 5, respectively. The G_d could not be extrapolated from the molecular weight range of 10–200 kGy since the plot of $1/\mathrm{Mn}-1/\mathrm{Mn}_0$ with dose does not give a straight line. Thus, a lower absorbed dose range (0.5 kGy–6 kGy) was then used to evaluate the G_d. The susceptibility of aqueous carrageenan to radiation degradation was also almost the same for all types of carrageenan; $G_d = 1.2$, 1.1, and 1.0×10^{-7} mol/J for κ-, ι-, and λ-carrageenan, respectively. Previous results using 4% solution gave almost the same G_d values for the different types of carrageenan. The values are lower than G_d obtained in current results with G_ds = 0.3, 0.5, and 0.5×10^{-7} mol/J for κ-, ι-, and λ-carrageenan, respectively (Relleve et al., 2005) probably due to the presence of sodium salts. Values of G_d for chitosan, alginate and galactomannans both in aqueous and solid form vary as shown in Table 1. The variations may be due to different starting materials, e.g. differences in Mw, purity, conformational state, degree of deacetylation, etc. In general, it can be seen from this table that G_d of purified κ-, ι-, and λ-carrageenan both in solid and aqueous forms is higher than other polysaccharides. This implies that pure carrageenans are more susceptible to radiation degradation than these other polysaccharides.

3.2. UV–vis spectrum

UV–vis spectrum of irradiated carrageenan shows a new absorbance peak at 260 nm (Fig. 4A shows only aqueous ι-carrageenan) for all types of carrageenan. This peak has been attributed to the formation of carbonyl group or double bond in the pyranose ring (Nagasawa, Mitomo, Yoshii, & Kume, 2000; Ulanski & Rosiak, 1992). The plot of the absorbance at 260 nm with increasing radiation dose is shown Fig. 4B. Irradiated solid carrageenans increased slightly their absorbance as a linear function. No difference in intensity was observed for the different types of carrageenan. In aqueous solution, increase in absorbance of ι-carrageenan was almost the same as λ-carrageenan but higher than κ-carrageenan. This observation is similar to results done previously using 4% carrageenan (Relleve et al., 2005). A linear curve was seen up to a dose of 100 kGy but which started to level off at 200 kGy.

3.3. FT-IR spectrum

FT-IR spectra in Fig. 5 show the finger print functional groupings of the carrageenans (Prado-Fernández, Rodríguez-Vázquez, Tojob, & Andrade, 2003) and some changes with irradiation. Similar spectrum has been obtained with low molecular weight κ-carrageenan processed by acid hydrolysis (Jiang, Guo, & Tian, 2005; Rochas, Rinaudo, & Vincendon, 1983). The spectra of κ-, ι-, and λ-carrageenan irradiated at 100 kGy in powder form indicated that their functional groupings were entirely kept intact even at a high dose of 100 kGy. Appearance of new absorption band at 1728 cm^{-1} was seen. This peak corresponds well to the increase in UV absorbance at 260 nm suggesting the formation of carbonyl group. On the other hand, more changes in the functional groupings were observed at 1% aqueous solution carrageenan irradiated at increasing doses from 2 kGy to 100 kGy. Increasing carbonyl peaks was observed with increasing doses. At 2 kGy, the finger print functional groups of all carrageenans were also kept intact. The spectra of the carrageenans started to be distorted at 10 kGy with a decrease in polymer bound water. These distortions were more obvious for ι- and λ-carrageenan with the increase in intensity and shifting of the 964–1200 cm^{-1} peaks (galactopyranose ring, glycosidic linkage) toward a higher wavelength, loss of peaks corresponding to covalent sulfate, 3,6 anhydro bridge (none for λ-) and D-galactose-4-sulfate. These distortions were seen at a higher dose of

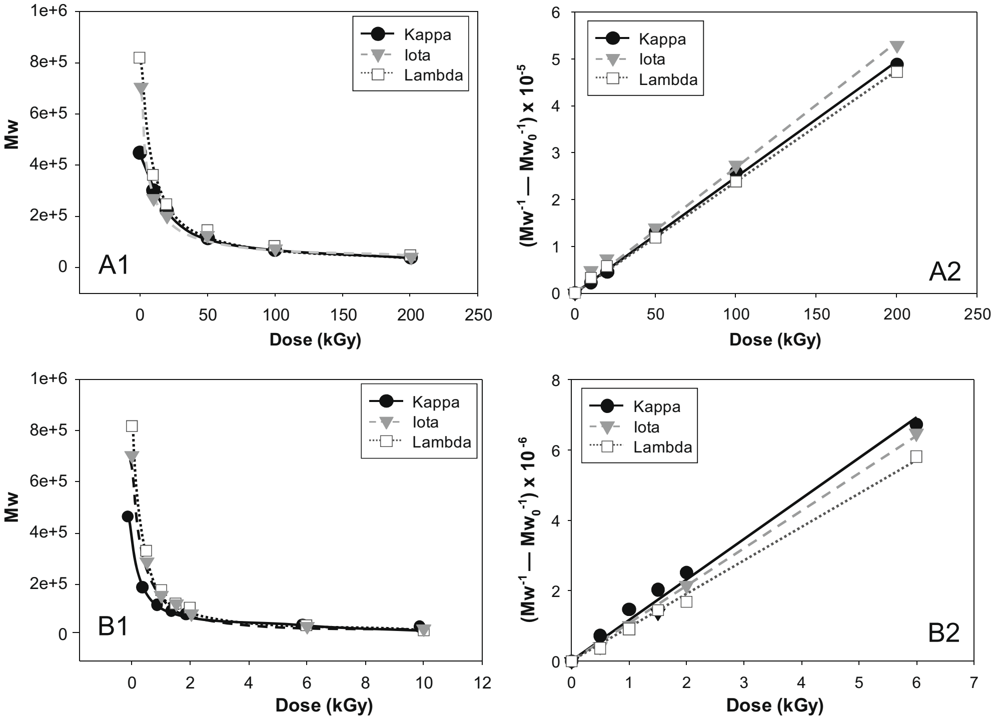

Fig. 3. Weight average molecular weight (Mw) and reciprocals of Mw of κ-, ι-, and λ-carrageenan irradiated at various doses in (A) solid and (B) 1% aqueous solution.

Table 1
Radiation degradation yield of different polysaccharides irradiated in solid and aqueous solution.

	G_d ($\times 10^{-7}$ moles/joule)		
	Solid	4% aqueous	1% aqueous
κ-Carrageenan	1.3[f] **2.5**	0.3[f]	**1.2**
ι-Carrageenan	1.0[f] **2.7**	0.5[f]	**1.1**
λ-Carrageenan	1.3[f] **2.3**	0.5[f]	**1.0**
Chitosan	6.0[a] 1.8[d] 0.9[d]		3.53[e]
Galactomannans	0.9–1.1[b]		
Alginate	1.9[c]	0.7[c] 0.1[e]	0.6[c] 0.8[e]

[*] Bold numbers refer to the current results.
[a] Czechowska-Biskup, Rokita, Ulanski, and Rosiak (2005).
[b] Sen, Yolacan, and Guven (2007).
[c] Nagasawa et al. (2000).
[d] Hai, Diep, Nagasawa, Yoshii, and Kume (2003).
[e] Wasikiewicza, Yoshii, Nagasawa, Wach, and Mitomo (2005).
[f] Relleve et al. (2005).

100 kGy for κ-carrageenan. Among the carrageenans, λ-carrageenan had the highest effect with an increase in the intensity peak at 964–1200 cm^{-1} at 100 kGy solid and at a low dose of 2 kGy aqueous solution.

3.4. Chemical analyses

Fig. 6 presents the dose dependence of the concentration of reducing eng groups for carrageenan at different irradiation conditions. The yields of radiolytically formed reducing groups, i.e. carbonyl groups, increased with increasing doses for all types of solid carrageenan. The increase in reducing end groups was almost the same for κ-, ι-, and λ-carrageenan. Free carbonyl groups in carrageenan macromolecule are formed in two ways, First, by radiolytically induced cleavage of glycosidic bonds, and second, as the result of oxidation of carbohydrate radicals generated inside the carrageenan residue. Obviously, aqueous carrageenans yielded more reducing end groups as more radiolytically formed reducing groups are expected from the indirect effect of OH radicals. Maximum amount of reducing sugars was obtained at 50 kGy, 20 kGy, and 2 kGy for κ-, ι-, and λ-carrageenan, respectively. Beyond this dose, oxidation of these reducing groups may have resulted in

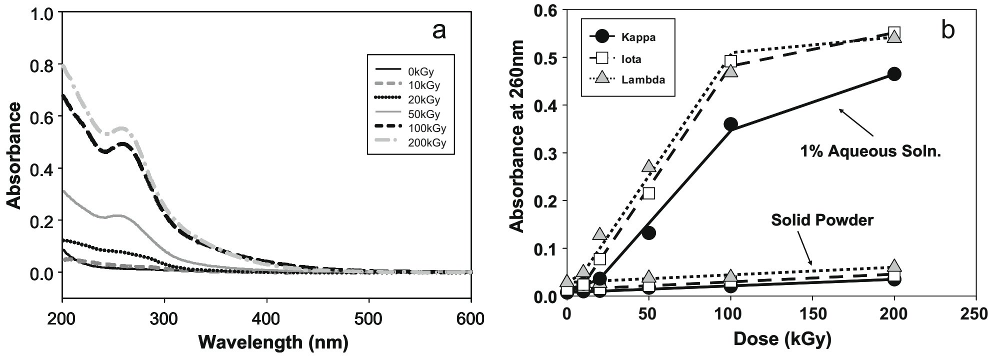

Fig. 4. (a) UV spectra of 1% aqueous solution of ι-carrageenan irradiated at various doses, (b) absorbance intensity of irradiated carrageenans at 260 nm.

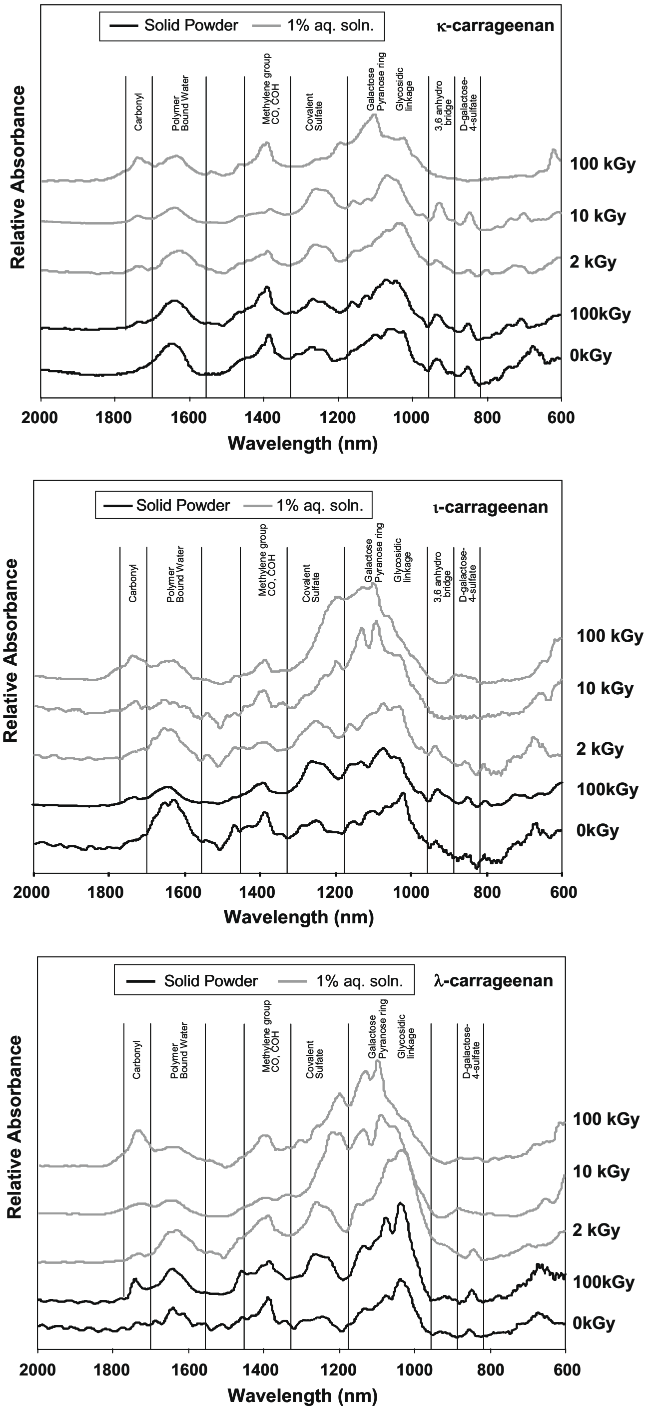

Fig. 5. FT-IR spectra of κ-, ι-, and λ-carrageenan in solid and at 1% aqueous solution at varying doses.

the formation of carboxylic acids. Further oxidation leads to decomposition products as observed by the darkening (yellow) of the solutions with increasing dose. These differences in maximum dose may have been influenced by the increase in acidity generated by free sulfates with increasing dose with λ- > ι- > κ-carrageenan. Among the carrageenans, κ- had the highest increase in reducing sugar. Iota had the least increase in reducing sugar. A study on the rate constants for the acid hydrolysis of κ-carrageenan in the disordered state indicate about 5–6 times higher than the value of ι-carrageenan which was explained by the stabilisation of the 3,6-anhydrogalactose linkage in ι-carrageenan by the sulfate groups in 2-position (Hjerde, Smidsrød, & Christensen, 1996).

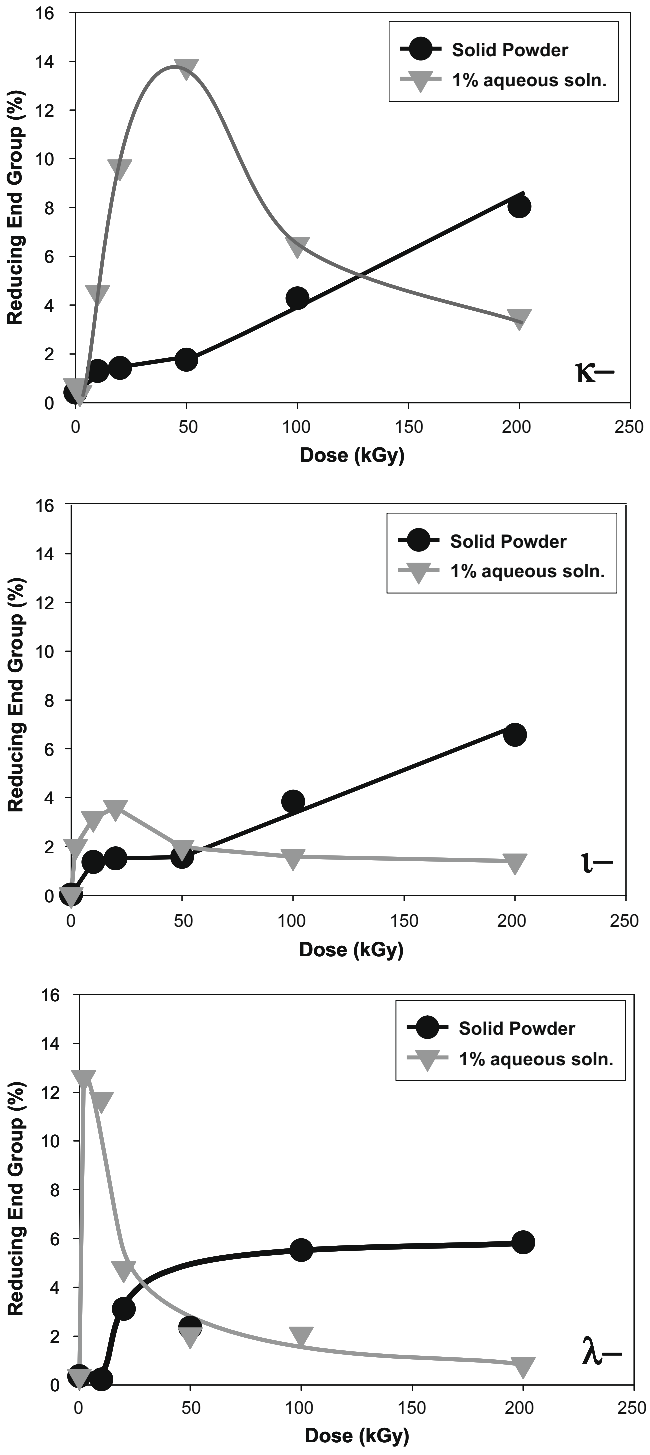

Fig. 6. Percent reducing group in κ-, ι-, and λ-carrageenan in solid and at 1% aqueous solution at varying radiation doses.

Sulfated galactans like carrageenans are known to release their sulfates after degradation (Karlsson & Singh, 1999; Millar & Blunt, 1998; Volpi, Mucci, & Shenetii, 1999) rendering them acidic. Fig. 7 shows a slight increase in acidity with solid carrageenans. Irradiation in aqueous solution, on the other hand, showed a marked increase in acidity up to 50 kGy. No further increase was observed beyond this dose for both κ- and ι-carrageenan. Lambda carrageenan showed a further slight increase in acidity beyond 50 kGy though it started to plateau at this dose. Lambda carrageenan had the highest acidity. These data coincide well with the expected release of sulfates from their number of sulfate groups (λ- > ι- > κ-

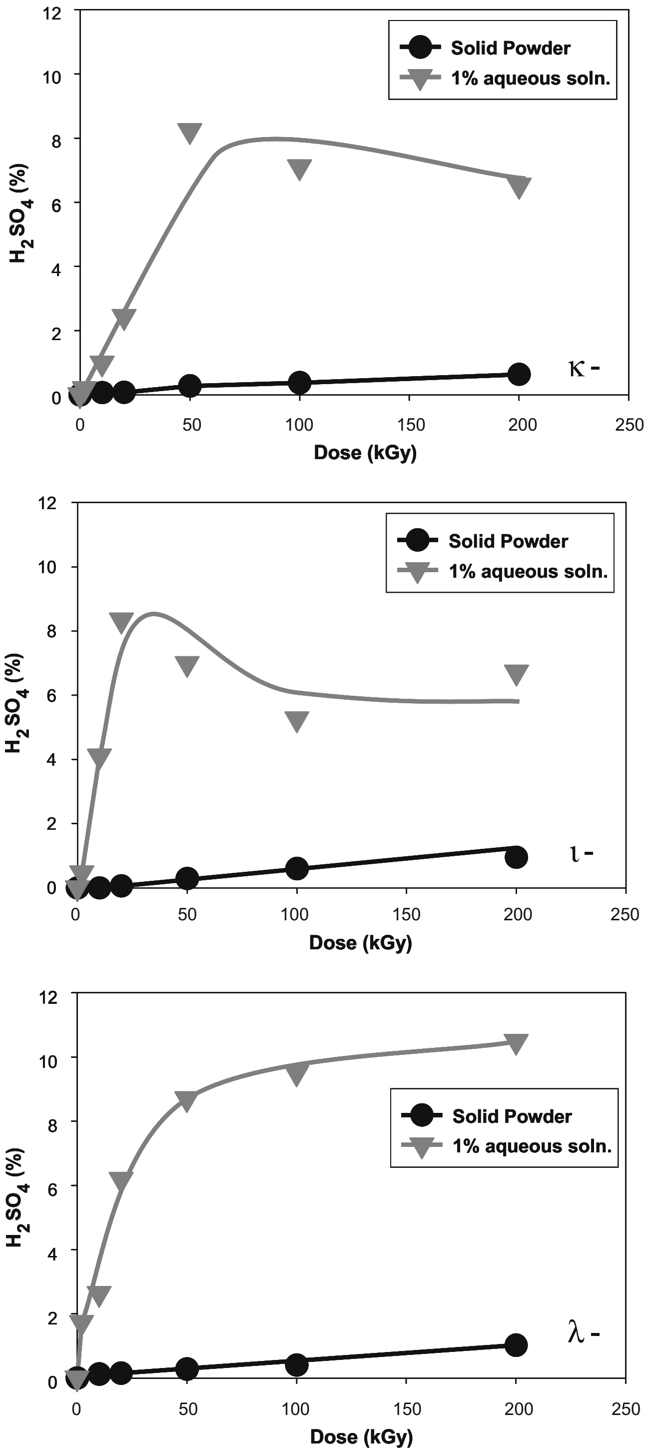

Fig. 7. Percent acidity (as H_2SO_4) in κ-, ι-, and λ-carrageenan in solid and at 1% aqueous solution at varying radiation doses.

). The order of sulfate release also agreed with what has been reported previously though desulfation effect is said to cease at a lower dose of 10 kGy for 4% gel state carrageenan (Relleve et al., 2005). Since the source of acidity of irradiated carrageenans does not originate only from the cleaved sulfates but also from the carboxylic groups formed, it would be interesting to know how much of the acidity is contributed by these groups. Based from the UV–vis absorbance at 260 nm, carbonyl groups still increased sharply beyond 50 kGy. Thus, the carboxylic groups may just have a minor contribution to the acidity of the carrageenans.

Several schemes for the radiation degradation of polysaccharides have been proposed by several authors, e.g. chitosan (Ulanski & Rosiak, 1992; Ulanski & Von Sonntag, 2000), pectin (Zegota, 1999), glucose (Phillips & Moody, 1959). Based on results of the spectral and chemical analyses of irradiated carrageenan, these schemes can be adopted to carrageenan. A possible mechanism for the radiation degradation of carrageenan can then be as follows:

Irradiation in solid:

$$R{-}H \rightsquigarrow R^{\cdot}(C_1{-}C_6) + H^{\cdot} \tag{3}$$

$$R{-}H + H^{\cdot} \rightarrow R^{\cdot}(C_1{-}C_6) + H_2 \tag{4}$$

$$R^{\cdot}(C_1,\ C_4) \rightarrow F_1^{\cdot} + F_2 \ \text{(scission)} \tag{5}$$

$$F^{\cdot} \rightarrow R(C{=}O) \tag{6}$$

Irradiation in aqueous solution:

$$H_2O \rightsquigarrow {}^{\cdot}OH + H^{\cdot} + e^-_{aq} \tag{7}$$

$${}^{\cdot}OH(H^{\cdot}) + RH \rightarrow R^{\cdot}(C_1 - C_6) + H_2O(H_2) \tag{8}$$

$$R^{\cdot}(C_1, C_4, C_5) \begin{cases} \rightarrow F_1^{\cdot} + F_2 \ \text{(hydrolysis)} & (9) \\ \rightarrow F_3^{\cdot} + F_4 \ \text{(scission)} & (10) \end{cases}$$

$$F_1^{\cdot}(F_3^{\cdot}) \rightarrow R(C{=}O) \text{ or } R(COOH) \tag{11}$$

$$2R^{\cdot}(F^{\cdot}) \rightarrow 2R(F) \ \text{(disproportionation)} \tag{12}$$

Irradiation in solid or aqueous solution (with oxygen):

$$R(C_1{-}C_6) + O_2 \rightarrow ROO^{\cdot} \rightarrow R(C{=}O) \tag{13}$$

$$ROSO_3^- + H^{\cdot} \rightarrow ROH + HSO_3^- \tag{14}$$

4. Conclusion

The radiation degradation yield of κ-, ι-, and λ-carrageenans irradiated in solid and at 1% aqueous solution at atmospheric conditions were almost the same for all types of carrageenan. G_d was in the range of $2.3–2.7 \times 10^{-7}$ mol/J and $1.0–1.2 \times 10^{-7}$ mol/J for solid and aqueous state irradiation, respectively.

UV and FT-IR spectral analyses indicated increasing carbonyl peaks with increasing doses for both solid and aqueous irradiation. Distortion of the carrageenan FT-IR finger print regions were observed starting at 10 kGy aqueous solution. These finger print regions were still intact up to a dose of 100 kGy for solid irradiation and 2 kGy for aqueous solution irradiation.

Chemical analyses indicated increasing reducing sugars for carrageenans with increasing doses and reached a maximum at a certain dose for the aqueous solutions. Kappa carrageenan showed the highest increase in reducing sugar. The carrageenans increased acidity with radiation dose due to the release of free sulfates. Lambda carrageenan had the highest increase in acidity.

The known dose of 100 kGy in solid form to obtain optimum biological activity may be reduced to a dose of 2–10 kGy using 1% aqueous solution. The molecular weights at these doses were equivalent to or lower than the Mw obtained at 100 kGy solid and the chemical structure of carrageenan at these doses remained intact. This information would be considerably useful especially in looking at the economics for the production of carrageenan oligomers by radiation processing.

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