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The effect of environmental humidity on radiation-induced degradation of carrageenans

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ABSTRACT

Better understanding of the chemistry of radiation-induced degradation is becoming of increasing importance on account of the utilization of polymeric materials in a variety of radiation environments as well as beneficial uses of degraded polymers. In this report the importance of environmental humidity on the degrading effect of radiation has been considered from the point of view of controlling the molecular weights of kappa- and iota-carrageenans. These two polysaccharides were irradiated in solid form under strictly controlled environmental humidity conditions by incubating and later irradiating the samples over saturated aqueous salt solutions of NaCl, $NaNO_3$ and $MgCl_2$. The degradation was followed in detail by a careful gel permeation chromatographic analysis of their respective molecular weights before and after irradiation. The chain scission yield values $G(S)$ were found to decrease with the water adsorbed from environment at every absorbed dose in the range of 5–100 kGy. On the other hand at very high water uptakes the yield of chain scission again increases especially at low doses. The decrease in degradation yield was attributed to the plastifying effect of water trapped in between the polymer chains facilitating the macroradical recombinations thus reducing the extent of chain scission. This study showed that although carrageenans were irradiated in solid form, the difference in their water uptake from changing environmental humidity has a profound effect in controlling their molecular weights by irradiation with ionizing radiation.

1. Introduction

Among various techniques used for the modification of polymer properties the use of ionizing radiation either in photonic (gamma rays, X-rays) or particulate forms (accelerated electrons, ion beams) has proven to be very convenient and versatile for large scale applications. Since the ultimate properties of polymers are generally controlled by their molecular weights, the control of molecular weight and its distribution is of great importance in determining the technical specifications required for a particular end-use. The polymers find their wide utilization in everyday life due to their light weights, relative ease of fabrication in the final form and unequalled mechanical properties based on performance vs. weight. The improvement in mechanical properties is mostly achieved by increased molecular weights and/or cross-linking of polymer chains. The increased resistance to heat, deformation and mechanical stresses obtained through radiation-induced cross-linking has long been the main reason for the use of high energy radiations in polymer processing (Haji-Saeid, Sampa, Ramamoorthy, Güven, & Chmielewski, 2007).

The opposite effect of radiation, in other words chain scissioning or degradation of polymers has not found great industrial interest until recently (Hien et al., 2000; Relleve et al., 2005; Şen, Yolaçan, & Güven, 2007). The degradation effect of ionizing radiation has been generally connected with the chemical structure of polymer chains, presence or absence of some additives and irradiation atmosphere, presence of oxygen or air leading mostly to radiation-induced oxidation with eventual chain scission. In recent years, there has been growing interest in understanding the effect of ionizing radiation on the chemical structure of polysaccharides such as chitin, chitosan, sodium alginate, and kappa carrageenan due to their versatile food and non-food applications (Choi, Ahn, Lee, Byun, & Park, 2002; Nagasawa, Mitomo, Yoshii, & Kume, 2000). The research in this field is mostly concentrated on the degradative effect of radiation to produce polysaccharides with desired low molecular weight ranges. The main effect of ionizing radiation on polysaccharides is chain scission of C—O bond connecting the glycoside groups on the main chain.

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Table 1
Water uptake of carrageenans incubated for 3 days in different humidity conditions.

Saturated solution (30 °C)	Atmospheric humidity (%)	Water adsorbed by KC (w%)	Water adsorbed by IC (w%)
$MgCl_2$	50	5	2
NaCl	75	21	17
KNO_3	90	40	31
Water	100	230	150

The three well known marine based polysaccharides namely, carrageenans, alginate and chitin/chitosan are known to be susceptible against ionizing radiation and degrade when irradiated in dry form or in solution. Some studies on irradiation of highly concentrated (>10%) solutions of carboxylate–polysaccharides in paste-like conditions have shown that chain scission is reduced in favor of crosslinking to from insoluble gels (Yoshii et al., 2003). The dependence of effect of radiation on the concentration of aqueous polysaccharide solutions prompted us to consider the effect of environmental humidity which may change from 0 to 100% depending on the climatic conditions, on radiation-induced degradation of this group of natural polymers.

2. Experimental

Commercially available kappa-carrageenan (KC) and iota-carrageenan (IC) were obtained from Aldrich and used as received. The CAS number of kappa-carrageenan (Type III) is 11114-20-8 and it is a mucopolysaccharide obtained from the cell walls of the red algae *Eucheuma cottonii*. The CAS number of iota-carrageenan (Type II) is 9062-07-1. The ion concentrations of KC used in this study are as follows: K^+, 11.3%; Na^+, 1.0%; Ca^{2+}, 2.2% (Aldrich Data Sheet, Lot (17327JI) results). The ion concentrations of IC are given as K^+, 4–6%; Na^+, 1–2%; Ca^{2+}, 2–4% (Sigma-Aldrich C1138 Specification Sheet).

In order to irradiate the polysaccharides mentioned above under controlled humidity conditions, saturated aqueous salt solutions were prepared from NaCl, $NaNO_3$ and $MgCl_2$ whose vapor pressures provide a certain constant humidity. In Table 1 given below relative humidity of the atmosphere above respective salt solutions are listed. The polysaccharide samples in powder form first dried in a vacuum oven at 40 °C and then placed in small baskets suspended over the saturated salt solutions all together kept in closed containers. The powders kept for three days in various constant relative humidity were thus allowed to absorb corresponding amounts of water by reaching equilibrium, all at room temperature. Water uptake of polymers determined gravimetrically corresponding to different environmental humidity levels was also indicated in Table 1.

The carrageenan samples equilibrated under different relative humidity of surrounding atmospheres and kept suspended over the salt solution were placed in tightly closed containers and irradiated to various doses (2.5, 5, 10, 20, 50 and 100 kGy) in a Gammacell 220 type ^{60}Co-gamma irradiator at room temperature in air at a dose rate of 0.18 kGy/h.

Irradiated and unirradiated samples were analyzed by a Waters Breeze model Gel Permeation Chromatograph equipped with an inline degasser (Waters AF) and a refractive index detector (Waters 2414). The mobile phase was 0.1 M $NaNO_3$ at a flow rate of 0.8 mL/min, and the columns were operated at 40 °C. The injection volume and concentration of injected polymer were 200 μL and 0.01 g/mL, respectively. 2000–1000–500 waters hydrogel columns were used to provide separation within a molecular weight range of 20,000–600,000. Universal calibration was constructed by using narrow molecular weight (20,600–553,000) PDI ≤ 1.04 standard samples of poly(ethylene oxide) obtained from PSS company. The Mark–Houwink constants used for PEO were $K = 6.9 \times 10^{-5}$ dL/g and $a = 0.81$ (Brandrup & Immergut, 1989). Corresponding constants for carrageenans were taken as $K = 5.98 \times 10^{-5}$, $a = 0.90$ (Zhou, Yao, & Wang, 2006) for use in universal calibration. The K and a constants of carrageenans used in this study was reported by Zhou et al. for 0.1 M KCl solution. The mobile phase used in GPC was however, 0.1 M $NaNO_3$ therefore we checked the elution behavior of KC in 0.1 M KCl and 0.1 $NaNO_3$ solutions and obtained the same chromatograms. Therefore we were confident to use these constants as the K and a constants of carrageenans of the eluting solvent of GPC i.e. 0.1 M $NaNO_3$ solution.

3. Results and discussion

3.1. Controlling the molecular weight of polysaccharides

It is very well known that polysaccharides in dry form or in solution degrade when exposed to ionizing radiation (Choi et al., 2002; Wasikiewicz, Yoshii, Nagasawa, Wach, & Mitomo, 2005). The results reported so far on the radiation-induced degradation of polysaccharides indicated that chain scission yield strongly depends on the concentration of polymer. In dilute aqueous solutions with polymer concentration less than 4% (w/v) the dominating effect is chain scission. The same applies to polysaccharides irradiated in solid state where radiation induced degradation yield, $G(S)$ defined as number of chain scissions per Joule of absorbed dose, reported for kappa-, iota- and lambda-carrageenans irradiated in solid form are within 0.104 μmol/J to 0.135 μmol/J range whereas for 4% solution the $G(S)$ values change from 0.83, to 1.24 and 1.35 μmol/J, respectively, for the three carrageenans mentioned above (Relleve et al., 2005). Since different units for the yield values are used in the literature, the $G(S)$ values given above were converted to μmol/J by multiplying the scission/eV(sc/eV) values by 0.10364, and concentration of the solution was also considered in the equations (Woods & Pikaev, 1994). In the study of Nagasawa et al. (2000), alginates were claimed to be more sensitive to degradation by irradiation though the $G(S)$ value for solid state irradiation was found to be similar to that of carrageenans, 0.2 μmol/J (1.9 sc/eV), in 1% aqueous solution the chain scission yield increased to 5.7 μmol/J (55 sc/eV), which reduced to 1.9 μmol/J (18 sc/eV) as a result of raising the solution concentration from 1 to 4%. In the calculation of G values reported above; however, the concentration of the solution was not considered. Taking into account the concentration effect as described by Janik, Kasprzak, Al-Zier, and Rosiak (2003) the corrected $G(S)$ values were recalculated in the recent study of Duy, Phu, Anh, and Hien (2011). As a result of recalculations, it was found that the $G(S)$ values should be 0.057 and 0.076 μmol/J for 1 and 4% alginate concentrations, respectively. These results clearly indicated that the $G(S)$ value increased with increasing polymer concentration in dilute regime. The effect of concentration on the radiation-induced degradation of chitosan, was explained in the recent paper of Duy et al. (2011) in detail. On the other hand, it has been shown that when the concentration of chemically modified polysaccharides, such as carboxymethylstarch, carboxymethylcellulose, carboxymethylchitin, and carboxymethylchitosan is increased beyond viscous solution to a paste-like condition, the crosslinking effect starts to dominate and typically chitosan a predominantly scissioning type of polysaccharide behaves like a crosslinking type upon carboxymethylation exhibiting approximately 60% gelation. (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Yoshii et al., 2003; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003).

It is very well known that the difference observed on the effect of radiation on polymers irradiated in dry or solution form is due

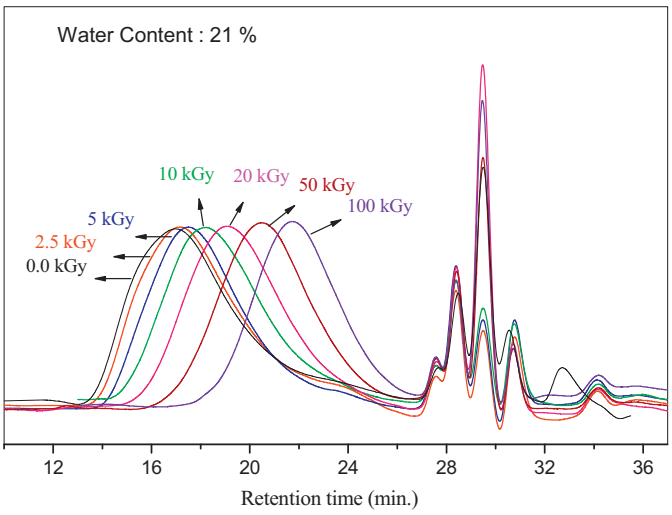

Fig. 1. Normalized GPC chromatograms of KC irradiated in 75% relative humidity (equivalent to 21% adsorbed water) to indicated doses.

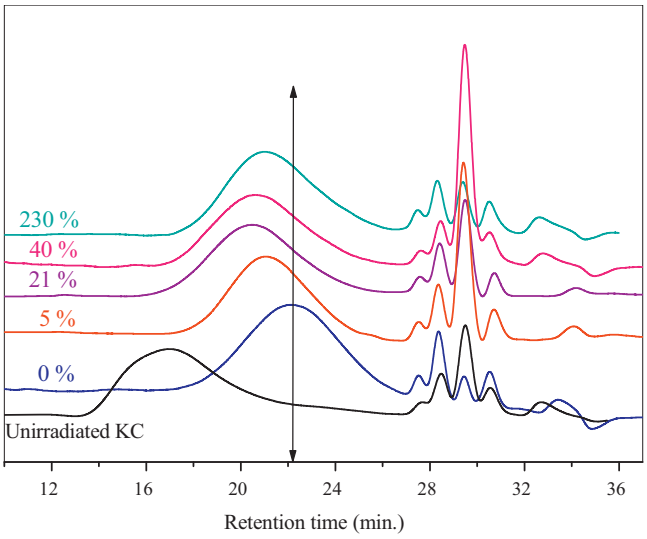

Fig. 2. The changes in molecular weight distribution of KC irradiated to 50 kGy dose at different levels of water uptake from the environment. The molecular weight distribution of unirradiated KC is given for comparison.

to indirect effect of radiation. In irradiations carried out in the presence of water the radiolysis products of water play the major role. In the above mentioned studies, a decrease of an order of magnitude in the molecular weights was observed as a result of the irradiations carried out in aqueous solutions and this was because of the secondary reactions taking place between the polysaccharides and the radiolysis products of water, mainly OH radicals.

The strong effect of the presence of water on the ultimate effect of irradiation of polysaccharides has leaded us to consider the effect of environmental humidity on the radiation chemistry of polysaccharides. We therefore decided to irradiate the carrageenan samples under different but well-defined and controlled environmental humidity conditions. For this purpose saturated solutions of certain salt solutions were prepared whose water vapor pressures hence surrounding equilibrium humidity levels are very well known as reported in Table 1. As briefly explained in the experimental section, polysaccharide powders placed in open mouth small baskets were suspended over the saturated salt solutions, all being kept in a closed container. Gravimetric studies showed that the equilibration of polysaccharide powders with surrounding humidity took 3 days. The polymer samples still being kept in the constant humidity chambers were irradiated in the Gammacell to required doses. The water uptake of carrageenan samples are indicated in Table 1.

Fig. 1 shows the normalized GPC chromatograms of KC containing 21% water (kept in 75% relative humidity) irradiated to doses indicated on the figure, from 2.5 to 100 kGy.

The overall effect of radiation as degradation is clearly seen from shifting of the chromatograms to lower molecular weight ranges with increasing dose. The small multiple after-peaks are due to some anions and cations present in KC and they act like internal standards in the chromatographic analyses of carrageenans (Şen, Yolaçan, & Güven, 2013). When KC kept at different humidity conditions and irradiated to the same dose, chromatograms obtained were observed to shift depending on the humidity. The sample chromatograms shown below in Fig. 2 are for KCs irradiated to 50 kGy at different humidity. GPC chromatogram of unirradiated KC is included in the same Fig. for comparison. A close look on the peak molecular weights shows that for the same absorbed dose chromatograms shift to lower elution volumes indicating an increase in molecular weight with increasing humidity content of the polymers.

These results show that presence of small amount of water in KC powders brings a big difference on the extent of radiation-induced chain scission. This can be more easily seen from Fig. 3 where $\bar{M}_n$ (g/mol) and $\bar{M}_w$ (g/mol) values of irradiated KCs are plotted against dose as a function of actual water content of polymers.

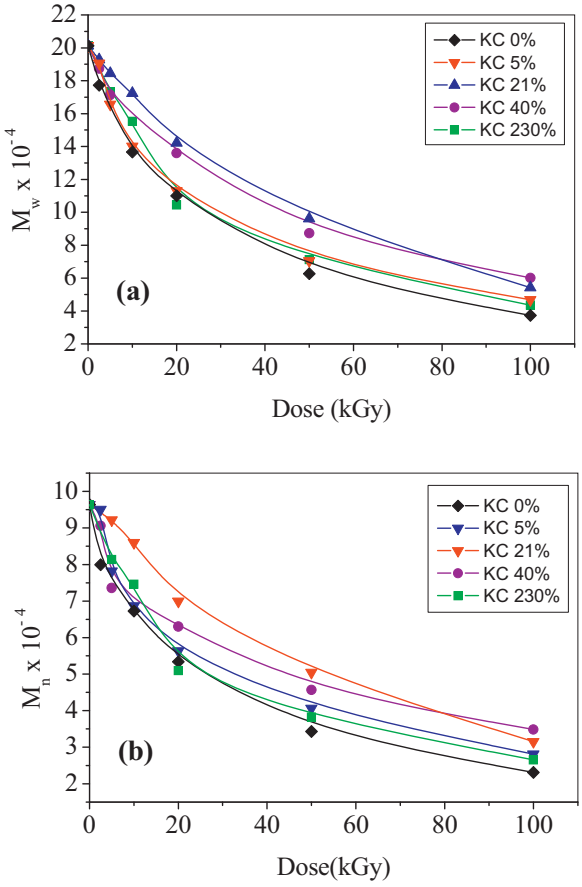

Fig. 3. The change of weight-average (a) and number-average (b) molecular weight of KC with different water contents as a function of dose. The amount of water content of KC is indicated in the inset.

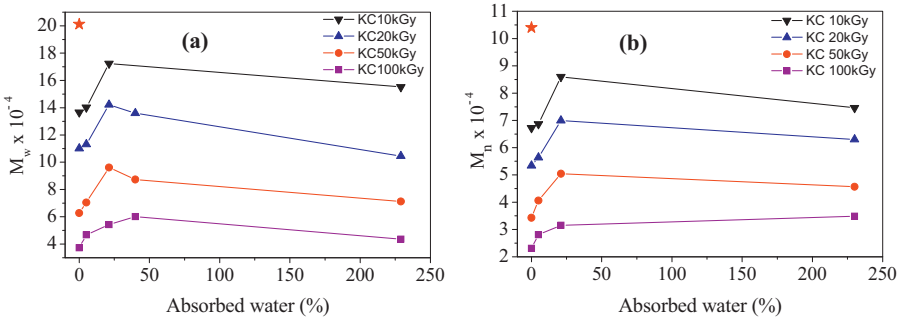

Fig. 4. The change in weight (a) and number-average (b) molecular weight of KC samples irradiated to 10–100 kGy doses at different water contents.

The information given in Fig. 3 can be better seen from Fig. 4 where the effect of small changes in the water content causes significant differences in radiation response of KC in terms of $\bar{M}_n$ values. As can be seen from Fig. 4, a KC sample irradiated to 20 kGy dose at 75% humidity shows equal $\bar{M}_n$ for the same KC irradiated to 10 kGy at 50% humidity. A target molecular weight can be achieved at half absorbed dose value by irradiating at reduced environmental humidity. From the economics of industrial radiation processing of these polysaccharides this brings a very big advantage. The molecular weights, $\bar{M}_w$ and $\bar{M}_n$ of unirradiated KC are indicated with an asterisk in Fig. 4.

3.2. Calculation of G(S) and G(X) from the molecular weights

Chain scissioning and crosslinking processes decrease or increase the molecular weights of polymer molecules, respectively. Therefore measurement of the changes in molecular weight averages and or distribution with dose can help to quantify these processes.

The change in number ($\bar{M}_n$) and weight ($\bar{M}_w$) and average molecular weights with dose for polymers irradiated in solution is determined by the relations given below (Charlesby, 1960):

$$G(S) - G(X) = \frac{c}{Dd}\left(\frac{1}{M_n} - \frac{1}{M_{n0}}\right) \quad (1)$$

$$G(S) - 4G(X) = \frac{2c}{Dd}\left(\frac{1}{M_w} - \frac{1}{M_{w0}}\right) \quad (2)$$

where c is the concentration of polymer in solution (g/dm^3); D is the absorbed dose (Gy); d is the solution density (kg/dm^3) and M values with subscript 0 refer to the respective quantities of unirradiated samples. The above equations are valid for polymers with initial most probable molecular weight distribution. (Charlesby, 1960). If scission only occurs then either Eq. (1) or (2) alone can be used to calculate $G(S)$ (Janik et al., 2003; Wasikiewicz et al., 2005). When both crosslinking and scission occur simultaneously $G(S)$ and $G(X)$ can be calculated from the simultaneous use of these two equations. If scission is the only mode of action of radiation then the radiation-chemical yield of degradation (scission) $G(S)$ (mol/J)can be determined from the following simplified equation:

$$G(S) = \frac{c}{Dd}\left[\frac{1}{\bar{M}_{n_D}} - \frac{1}{\bar{M}_{n_0}}\right] \quad (3)$$

In this study radiation-induced degradation of carrageenans was investigated in detail by a Gel Permeation Chromatographic analysis of their molecular weights before and after irradiation. The above mentioned equations were used in determining the radiation–chemical yields of degradation.

As it has been indicated above, in order to obtain quantitative information on chain scission yields, $1/\bar{M}_n$ and $1/\bar{M}_w$ vs. dose diagrams should be constructed according to Eqs.(1) and (2). When this is done Fig. 5 is obtained. From the overall slope of the lines, we calculated the $G(S)$ and $G(X)$ (μmol/J) values. The yield values determined for KC are listed in Table 2. As can be seen from the table, the mode of action of radiation on KC is dominantly chain scission. On the other hand, a small effect of crosslinking has been observed at 21% water-containing carrageenan.

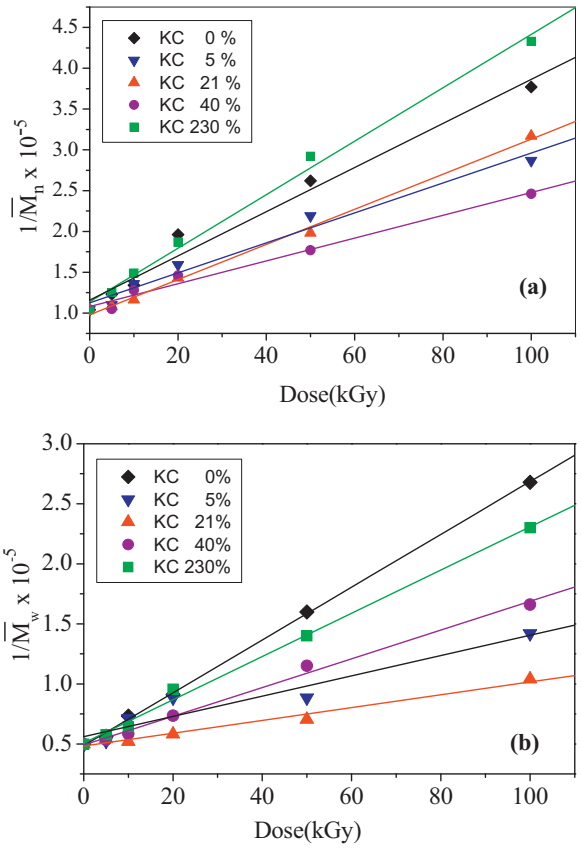

Fig. 5. (a) $1/\bar{M}_n$ and (b) $1/\bar{M}_w$ vs. dose plot for KC. The percentage of water content in KC is given as inset.

Table 2
Change of $G(S)$ and $G(X)$ with humidity for KC.

Adsorbed Water (%)	$G(S)$ (μmol/J)	$G(X)$ (μmol/J)
0	2.70	–
5	1.80	
21	2.57	0.37
40	1.54	–
230	0.99	–

Table 3
Change of individual G(S) values with humidity for KC as a function of dose.

Adsorbed water (%)	Absorbed dose (kGy)				
	5.0	10.0 $G(S)$ (μmol/J)	20.0	50.0	100
0	3.80	3.00	4.60	3.16	2.73
5	1.14	3.05	2.60	2.19	1.74
21	0.82	0.97	1.61	1.56	1.82
40	0.14	1.72	1.50	1.04	1.02
230	1.27	1.36	1.25	1.14	0.99

Table 4
Change of average number of bonds cleaved per original polymer molecule with humidity for KC as a function of dose.

Adsorbed water (%)	Irradiation dose (kGy)				
	5.0 (N)	10.0	20.0	50.0	100.0
0	0.183	0.288	0.885	1.519	2.625
5	0.058	0.308	0.529	1.106	1.760
21	0.038	0.115	0.375	0.904	2.048
40	0.010	0.231	0.404	0.702	1.365
230	0.202	0.433	0.798	1.808	3.163

Although it is possible to calculate an overall value for $G(S)$ from the slope of the lines in Fig. 5, we have preferred to calculate individual values of $G(S)$ as a function of humidity and dose by using Eqs. (1)–(3). The results thus obtained are collected in Table 3. The effect of presence of low level of water in solid KC on radiation-induced degradation is clearly seen from the $G(S)$ values listed in this Table. Degradation yield is the highest for dry irradiated samples and with water taken up from the atmospheric humidity degradation becomes less pronounced and $G(S)$ values show a decrease for a given dose. This finding of strong effect of small amounts of adsorbed water on decreasing the yield of degradation has very important implications on industrial radiation processing of these natural polymers. On the other hand, a decrease in the overall $G(S)$ value from 2.70 to 1.80 in 5% water-containing system Table 2, is very interesting given that there is no contribution coming from crosslinking, $G(X) = 0$. This can be analyzed by determining the number of bonds cleaved per original polymer molecule or self-repairing of the chains during irradiation.

In order to examine the effect of water on the radiation-induced degradation of carrageenans, the average number of bonds cleaved per original polymer molecule was also determined from the following equation:

$$N = \frac{\bar{M}_{n0}}{\bar{M}_{nD}} - 1 \qquad (4)$$

where M_{n0} and M_{nD} are the M_n values before and after irradiation at a certain dose (D), respectively and, N denotes the degree of scission. The N values calculated for KC are given in Table 4. As can be seen from the table, the N values increased continuously with dose and water content of the samples. For a given dose on the other hand, these values decreased up to certain water content in the polysaccharide structure, and then increased again at relatively high water levels. These results again clearly indicate that the bond cleavage in KC was significantly influenced by incorporation of small amount of water in the polymer structure.

The apparently dry polysaccharide samples may always contain certain amount of water which is directly related to the humidity of surrounding atmosphere of storage conditions. One therefore has to be very careful when irradiating polysaccharides in apparently dry form and their actual water contents should be known before and during radiation processing. Otherwise as shown in this study inconsistent value of molecular weights and/or scission yields might be reported for the same sample irradiated to the same dose if the environmental humidity conditions are different.

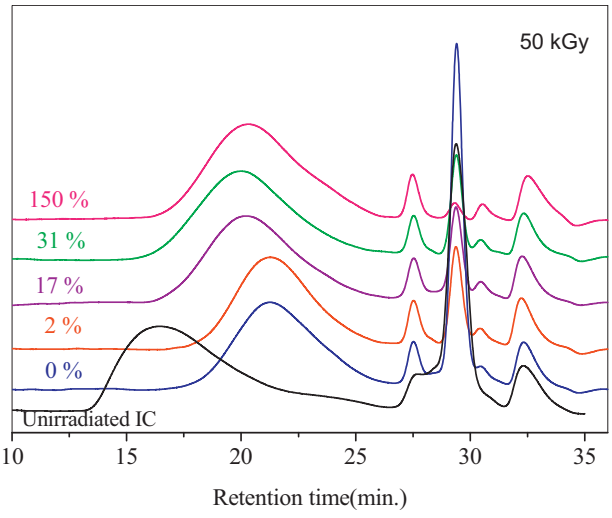

Fig. 6. GPC chromatograms of IC with various water contents irradiated to 50 kGy. GPC chromatogram of unirradiated IC is given for comparison.

Table 5
Change of $G(S)$ and $G(X)$ with humidity for IC.

Adsorbed water (%)	$G(S)$ (μmol/J)	$G(X)$ (μmol/J)
0	4.23	0.12
2	4.19	0.09
17	1.68	0.24
31	1.10	0.17
150	1.06	0.02

Table 6
Change of individual G(S) values with humidity for IC as a function of dose.

Adsorbed Water (%)	Absorbed dose (kGy)				
	5.0 $G(S)$ (μmol/J)	10.0	20.0	50.0	100.0
0	21.6	12.3	6.83	4.40	4.70
2	13.3	8.36	4.88	3.80	4.47
17	6.33	5.90	4.09	2.22	1.81
31	4.33	2.61	2.74	1.76	1.22
150	6.23	3.42	2.50	1.19	1.26

Expressed in a different way twice as much high dose might be needed to achieve the same final molecular weight of carrageenans if irradiated in an irradiation facility located in an environment of relatively high humidity.

Results very similar to those given for KC were also obtained for IC. The hydrophilicity of IC however was found to be less than that of KC as can be seen from the lower level of water taken up under exactly the same conditions. In Fig. 6 below, one can see the similar trend in changing of molecular weight distribution of IC irradiated to 50 kGy at varying humidity conditions. GPC chromatogram of unirradiated IC is also given for comparison purpose. Degradation effect is the highest for dry irradiated IC like in KC and with water taken up from the atmospheric humidity degradation becomes less and the molecular weight distribution curves shift to lower elution volumes corresponding to higher molecular weights. In order to obtain quantitative information on chain scission yields, $1/\bar{M}_n$ and $1/\bar{M}_w$ vs. dose diagrams were constructed in Fig. 7 according to Eqs. (1) and (2). From the overall slope of the linear parts of the curves, the $G(S)$ and $G(X)$ values (μmol/J) were calculated. The yield values determined for IC were given in Table 5. As it is seen from this table, and different from KC, the chain scission and crosslinking reactions occurred simultaneously for all the samples containing different levels of water. The effect of adsorbed water on the individual $G(S)$ values is presented in Table 6. The table clearly indicates

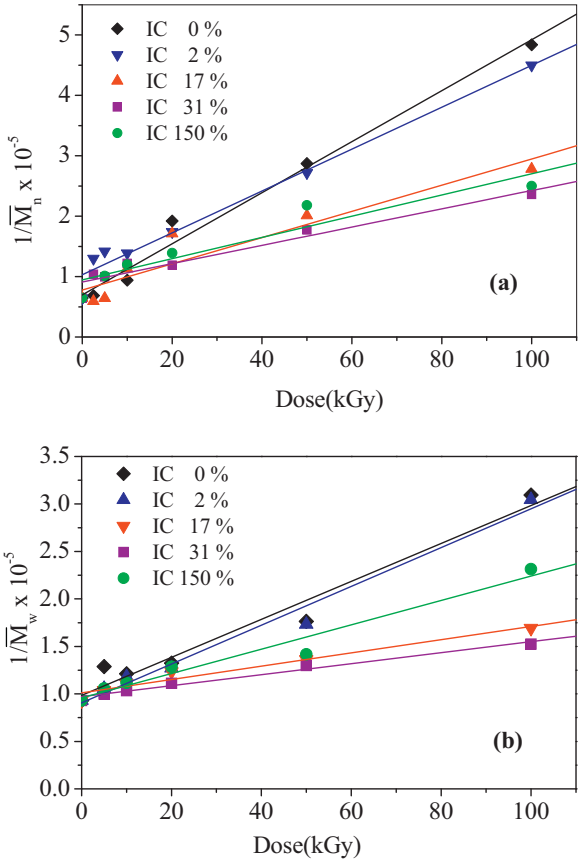

Fig. 7. (a) $1/\bar{M}_n$ and (b) $1/\bar{M}_w$ vs. dose plot for IC. The amount of water content in IC is indicated in the inset.

that with water taken up from the atmospheric humidity radiation-induced degradation became less pronounced, and the $G(S)$ values decreased. The $G(S)$ value was 21.6 (μmol/J) for 5.0 kGy-irradiated dry IC, and decreased gradually to 6.23 (μmol/J) with the increase of adsorbed water content to 150%, Table 6. The individual $G(S)$ values determined for IC were found to be higher than those of KC which is mainly due to the lower level of water taken up by IC.

When carrageenans are irradiated in dry form, the radicals generated on the main chains do not benefit from the segmental mobility of chains to encounter with each other to form crosslinks but suffer from chain scission. In dilute solutions however although chains are fully mobile, the probability of two radical sites on two separate chains to meet each other to reestablish a covalent bond is very small due to large distances involved between the polymer coils in the solution. The additional indirect effect of OH radicals from water radiolysis enhances the radical attacks on the chains with eventual increase in chain scissioning, especially in the presence of dissolved air (oxygen). The $G(S)$ values obtained from irradiations in aqueous solution are therefore much higher than those observed for solid state irradiations. Similar results have been amply demonstrated in the literature for other polysaccharides. When there is only small amount of water trapped in the polysaccharide structure however, like in this work, it is unlikely to expect an indirect effect of radiation. Small amount of water located in between the carregeenan chains however can reduce the interchain hydrogen bonding thus allowing enough mobility to kappa and iota carrageenan chains. Chain mobility enhanced by the plastifying effect of water may increase the combination of radicals on neighboring chains thus lowering the extent of degradation hence reducing $G(S)$ values. The increase in chain mobility due to plastifying effect of water layer should demonstrate itself in decreasing the glass transition of the humid polysaccharides. The effect of small amount of water or bound non-freezing water on the phase transition behavior of a series of guar gum–water system was investigated using differential scanning calorimetry by Naoi, Hatakeyama, and Hatakeyama (2002). Their conclusion was that the presence of bound, non-freezing water increase the mobility of the chains acting like a plasticizer. As a result of increase in chain mobility they observed approximately 20 °C decrease for the transition temperature of guar gum polysaccharide. This is a strong support of our explanation on the plasticizing effect of low level of water in polysaccharides. We were not however able to justify this experimentally by measuring the glass transition temperatures of carrageenans as a function of their water contents because of thermal degradation of samples upon heating.

4. Conclusions

Reduction of molecular weights of natural polymers in a controlled way is an important process for different uses of these polymers. Radiation processing being a room temperature process not requiring any additives can be considered as one of the most efficient tools in controlled degradation of polysaccharides. The degrading effect of ionizing radiation on carrageanans; however, has been shown to be very sensitive on the relative humidity of the irradiation environment. Solid powders of carrageenans with different small amounts of water taken up from the surrounding humidity show significantly different levels of degradation when irradiated to the same doses. Controlling of environmental humidity during storage and irradiation of these types of polysaccharides is therefore an important factor to be considered in industrial radiation processing.

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