M. Şen, P. Taşkın and O. Güven / Hacettepe J. Biol. & Chem., 2014, 42 (1), 9–21

Effects of polysaccharide structural parameters on radiation-induced degradation

Polisakkaritlerin yapısal parametrelerinin radyasyonla uyarılmış bozunmasına etkisi

Review Article

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ABSTRACT

Especially, in last decade considerable attention has recently been directed to the modification and preparation of low-molecular weight-fractions or oligosaccharides of kappa carrageenan, sodium alginate [1-4] and Chitosan [5-10] by radiation induced degradation in dry, and various concentrations in aqueous solutions in order to use mainly in the plant growth promoter, plant protectors and tissue engineering applications.

Neither in these radiation induced degradation studies of NaAlg, nor in other studies on the preparation of oligosaccharides of sodium alginate, Chitosan, galactomannans as the plant growth promoter and plant protectors [10-12] the effect of structural parameters of polysaccharide type natural polymers was considered by the authors. By the recent studies Şen et al., [13-15], this deficiency in the literature was filled and the effects of the structural parameters of some polysaccharide on the radiation-induced degradation are explained in details. All these recent studies are summarized in this review.

Key Words
Polysaccharide, radiation induced degradation, galactomannan, sodium alginate, chitosan.

ÖZET

Özellikle son on yılda kappa karragenan, sodyum aljinat [1–4] ve kitosan'ın [5–10] düşük molekül ağırlıklı fraksiyonlarının ya da oligosakkaritlerinin katı halde ve farklı çözelti derişimlerinde radyasyonla hızlandırılmış bozunma ile hazırlanması, modifikasyonu ve hazırlanan bu fraksiyonların bitki büyütme hızlandırıcısı, bitki koruyucusu olarak ve doku mühendisliği uygulamalarında kullanılmasına yönelik yoğun bir ilgi vardır.

Ancak ne polisakkaritlerin radyasyonla uyarılmış bozunma çalışmalarında ne de sodyum aljinat, kitosan, galaktomannan oligosakkaritlerinin bitki büyütme hızlandırıcısı ve bitki koruyucusu olarak hazırlanması konusunda [10-12] yapılan diğer çalışmalarda polisakkarit'in yapısal parametrelerinin etkisi konusu bugüne kadar yazarlar tarafından dikkate alınmamıştır. Şen ve arkadaşları tarafından yapılan son çalışmalarda [13-15] literatürdeki bu boşluk kapatılmış ve polisakkaritlerin radyasyonla uyarılmış bozunmasına yapısal parametrelerin etkisi ayrıntılarıyla açıklanmıştır. Yakın zamanda yapılan tüm bu çalışmalar bu derlemede özetlenmiştir.

Anahtar Kelimeler
Polisakkarit, radyasyonla uyarılmış bozunma, galaktomannan, sodium aljinat, kitosan.

Article History: Received September 18, 2013; Revised September 24, 2013; Accepted September 25, 2013; Available Online: February 5, 2014.

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INTRODUCTION

Recently, Nagasawa et al. [10] investigated the effect of radiation on alginates in solid state and in aqueous solution. It was found that NaAlg degraded after irradiation in both solid state and aqueous solution; and the degradation in solution was remarkably greater than that in the solid state. Degradation yields, (G(S)), of NaAlg were found in this study as 1.9 (scission/eV) (0.197 μmol/J) and 55 (scission/eV) (5.7 μmol/J) for solid state and aqueous solution, respectively.

In another study performed by Wasikiewicz et al. [11], ultrasonic, ultraviolet and gamma degradations of NaAlg and Chitosan were investigated. It was found for both polymers that the most effective method, from the energetic point of view, was gamma radiation with a yield of scission, G(S), of 0.55 x 10^{-7} mol/J for 1% alginate, and 3.53 x 10^{-7} mol/J for 1% chitosan. However, considering the reaction time, the ultraviolet method was the most effective, with the reaction rate constant, k, of 0.52 h^{-1} for alginate, and 1.6 h^{-1} for chitosan.

Considerable attention has recently, especially in the last decade, been directed to the modification and preparation of low-molecular weight-fractions or oligosaccharides of chitosan by radiation-induced degradation in dry-state or in aqueous solutions with various concentrations in order to use mainly in the plant growth promoter, plant protectors and tissue engineering applications [16-17].

In the literature the general consensus is that the irradiation state (dry or aqueous solution) and the presence of hydroxy generating groups and the initial molecular weight of chitosan are important factors in controlling its radiation induced degradation behavior. So far, nonetheless, no relationship has been established between the structural parameters of polysaccharide and radiation stability. In this review the effect of the structural parameters of some polysaccharides on the radiation-induced degradation is explained in details.

Effect of Mannose-to-Galactose ratio (M/G) on the Radiation Stability of Galactomannans

Galactomannans are neutral polysaccharides that occur in substantial amounts in the endosperm of the seeds of some leguminous plants. Structurally they consist of a β (1-4)-D-mannose backbone to which galactose units are attached α (1-6). Of the number of galactomannans known, guar gum (GG), locust bean gum (LBG), and tara gum (TG) are the most used in applications in, for example, the food, pharmaceutical, and chemical industries as thickening agents or stabilizers due mainly to the high viscosity they give at low w/w concentrations. While guar gum commonly has a mannose-to-galactose ratio (M/G) of approximately 2, M/G ratio is 3 and 4 for TG and LBG respectively [18]. Their functional and physical properties (including solubility, gelling behavior, and viscosity) are related to the molecular structure, sugar composition, degree and distribution of branching, and polymerization [19]. In many industrial applications, degradation of linear polysaccharides is essential.

For example, guar solutions, which are used as hydraulic fracturing fluids in oil and gas recovery, need to be degraded to facilitate the outflow of oil. In addition, to understand the solution properties of guar as well as other water-soluble biopolymers, it is often necessary to degrade the native polymer to prepare samples with various molecular weights (MW) [20]. Degradation of polysaccharides has been widely studied. Though acid and enzymatic hydrolysis [21-23] are most common, other methods such as thermal [20], γ-irradiation [24], extrusion, ultrasonication [23, 25] and free radical degradation are also reported [26].

However, mostly enzymatic hydrolysis is used to degrade galactomannans. There is only one work about degradation of guar gum with γ-rays in solution state. Jumel et al. [27] investigated the change of absolute molecular weight and viscosity properties of guar gum samples irradiated in solution state with gamma rays in a 0-10kGy dose range. They observed that the molecular weight and viscosity of the guar gum decreased with irradiation and this decrease was relatively steep at low irradiation doses (0.1-0.8kGy). The decrease was much slower at high doses in both molecular weight and viscosity. They also investigated the change in the number of chain breaks per molecule G(s). They concluded that G(s) values at the lower irradiation doses were higher than that at the higher irradiation doses, i.e. more molecules were affected by the low irradiation doses [27].

In the present study of Şen et al [13] GG, TG and LBG samples were irradiated in a gamma cell in the solid state. The changes in their molecular weights were determined by SEC analysis and the change in their viscosity values with change of temperature and irradiation dose were determined. G(s) and degradation rate values were calculated.

From the result of this study, The SEC chromatograms of LBG irradiated in the dose range of 2.5-75 kGy are given in Figure 1 as examples. Similar unimodal distributed chromatograms are obtained also for GG and TG samples. As the irradiation dose increased, the SEC chromatogram of the LBG sample is shifted to higher retention volumes indicating the molecular weight of the sample is decreased with irradiation.

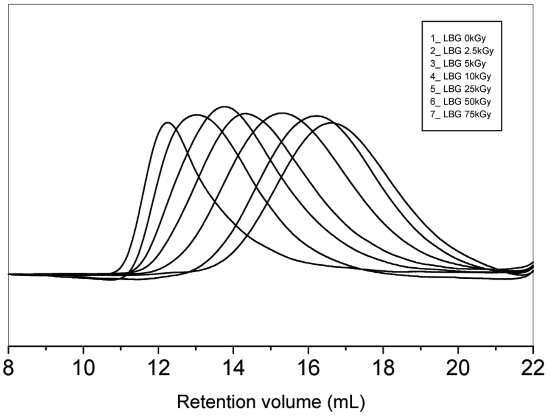

Figure 1. Size exclusion chromatograms of irradiated LBG.

The change of weight ($\overline{M}_w$) and number average ($\overline{M}_n$) molecular weights with irradiation dose is given in Figure 2 and 3, respectively. As can be seen from these two figures, both average molecular weights decrease rapidly until 50 kGy and then this decrease was slowed down at higher doses and almost the same final molecular weight value was reached by all galactomannan samples.

The efficiency of radiation-induced events is expressed by the so-called G-value. The G-value, equal to the number of events per 100 eV of energy absorbed or equal to the mol of events per J of energy absorbed, has customarily been used to measure the radiation chemical yield.

Molecular weight values of galactomannans are used for the determination of chain scission yield, (G(S)), crosslink yield (G(X)) and degradation rate. By using the related equations given in the literature [28] zero G(X) values were found for each galactomannan. If scission is the only mode of action of radiation then the radiation-chemical yield of degradation (scission) G(S) is determined from the Alexander-Charlesby-Ross equation [29].

$$\frac{1}{M_{n_D}} = \frac{1}{M_{n_o}} + 1.04 \times 10^{-7}\ G(S)D$$

Where the absorbed dose, D, is in kGy, $\overline{M}_{n_D}$ and $\overline{M}_{n_o}$ are the number average molecular weights of the polymer before and after irradiation,

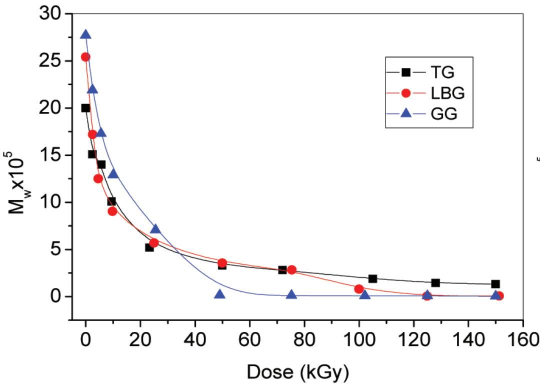

Figure 2. The change in weight average molecular weight ($\overline{M}_w$) of galactomannans with dose.

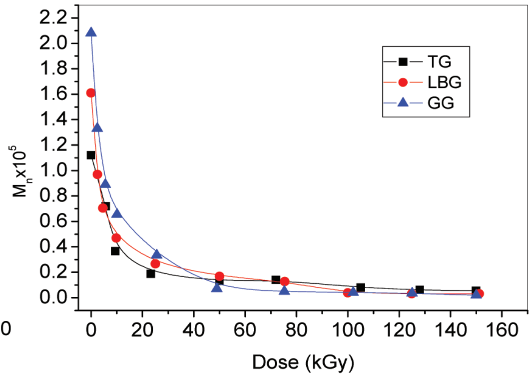

Figure 3. The change in number average molecular weight ($\overline{M}_n$) of galactomannans with dose.

respectively. For the determination of the G(s) values, $1/\bar{M}_n$ was plotted against dose for all samples and given in Figure 4. Then by using the slopes G(s) values were calculated. The calculated G(s) values is 0.113 ± 0.002, 0.111 ± 0.006, 0.088 ± 0.010 µmol/J for GG, TG and LBG, respectively. It is concluded that G(s) values are dependent on the structure (galactose-mannose ratio) of the sample and follows an order of GG > TG > LBG for these initial molecular weights. When the chemical structures of these gums are examined it is seen that GG has one galactomannan unit attached to the backbone per two monomeric units of the backbone. This is one per three monomeric units for TG and one per four monomeric units for LBG.

It can be concluded that the G(s) value increases with an increase in the galactose to mannose ratio and/or molecular weight of the unirradiated sample.

The equation given by Jellinek [30] is modified and used in the determination of degradation rate. Where N is the average number of bond cleavages per original polymer molecule, this value can be calculated by:

$$N = \frac{\bar{M}_{n_o}}{\bar{M}_{n_D}} - 1 \qquad (1)$$

Where, $\bar{M}_{n_o}$ and $\bar{M}_{n_D}$ are $\bar{M}_n$ at time zero and after irradiation to a certain dose (D), respectively.

N is also named the degree of scission. Assuming the rate of chain scission is independent of chain length and position of the link in the chain, N is anticipated to be a linear function of irradiation dose (first-order reaction)

$$N = \frac{\bar{M}_{n_o}}{\bar{M}_{n_D}} - 1 = k\left[\frac{\bar{M}_{n_o}}{m_o}\right] D \qquad (2)$$

Where, k is the rate constant and m_o is the molecular weight of a monomer unit. Eq. (2) can be rewritten as:

$$\frac{1}{\bar{M}_{n_D}} - \frac{1}{\bar{M}_{n_o}} = \left(\frac{k}{m_o}\right) D \qquad (3)$$

Degradation rate constants for GG, TG and LBG were determined by using the $(1/\bar{M}_n)$-$(1/\bar{M}_{n_o})$ vs. dose and given in Figure 5. Determined degradation rate constants for GG, TG and LBG are given in Table 1. It follows an order of GG > LBG > TG. These results clearly indicate that degradation rate is not completely independent of the initial chain length of the gum. As can be seen from Figure 2 and 3 the molecular weights of the gums also follow the same order. The authors conclude that as the galactose to mannose ratio and the original molecular weight increased, effect of irradiation on the molecular weight and rheological properties of the sample became more pronounced and the M/G ratio is one of the reasons affecting chain scission yield of galactomannans.

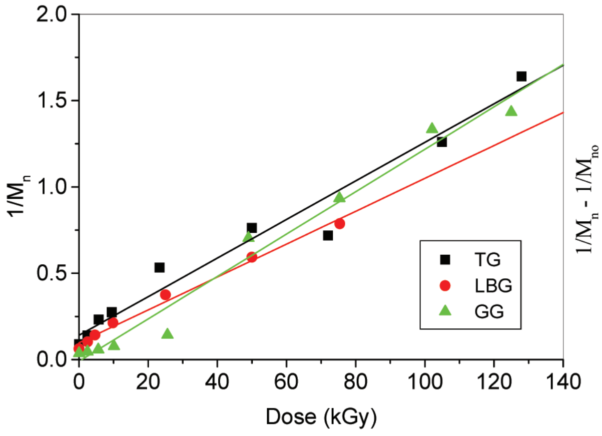

Figure 4. $1/\bar{M}_n$ vs. dose plot to determine G(S) values of GG, TG and LBG.

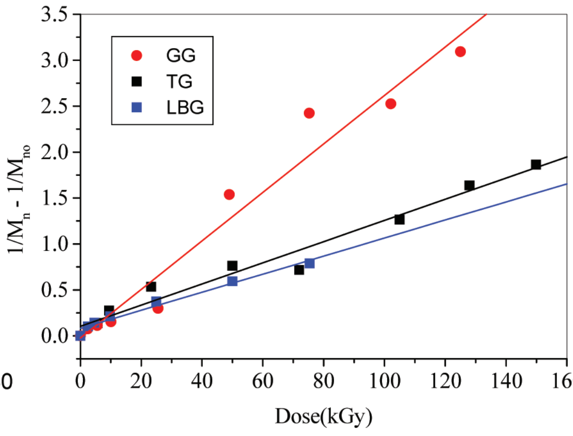

Figure 5. $1/\bar{M}_n$ - $1/\bar{M}_{n_o}$ vs. dose plot to determine degradation rate constants of GG, TG and LBG.

Table 1. Degradation rate constants of GG, TG and LBG

Polymer	Degradation Rate Constant (kGy^{-1})
LBG	12.90 ± 0.95
TG	7.45 ± 0.98
GG	7.93 ± 0.56

Effect of guluronic acid/mannuronic acid ratio (G/M) on the radiation-induced degradation of sodium alginate

Alginate is one of the natural polysaccharides that occur in substantial amounts in the brown seaweeds. Alginates are unbranched binary co-polymers of (1-4)-linked residues of β-D-mannuronic acid (M) and α-L-guluronic acids (G). Alginic acid and its water-soluble sodium salt have been manufactured for decades for their great ability to give highly viscous solutions even at moderate concentrations and mainly used in food, pharmaceutical, and chemical industries as thickening agents, drug carrier, stabilizers, and plant growth stimulator [1, 31-32]. Aqueous solution of sodium alginate forms stable gels in the presence of multivalent cations such as Ca^{2+} and Mg^{2+}. Gel formation occurs due to the ionic interaction between guluronic acid residues from two or more alginate chains and cations, yielding a three-dimensional network of alginate molecules well described by the "egg-box model" [33]. Functional and physical properties, mechanical strength, porosity, gel uniformity, biocompatibility, and influence on encapsulated cells properties of Alginate gels vary widely depending on ratio of mannuronic to guluronic acids, the frequency and size of guluronic acid blocks, the molecular weight of the polymer [34-35]. Experimental studies have shown that selective binding of certain alkaline earth metal ions increase markedly with increasing content of the α-L-guluronic acids (G) residues in the chain. On the other hand, poly-mannuronate blocks and alternating blocks are almost non selective.

Neither in these radiation induced degradation studies of NaAlg, nor in other studies on the preparation of oligosaccharides of NaAlgs as the plant growth promoter and plant protectors [10, 12]. The effect of configuration of NaAlg was considered by the authors. Radiation induced degradation of sodium alginate (NaAlg) having different G/M ratios was investigated for the first time Şen et al. [14].

From the results of this study, changes in the weight and number average molecular weights (Mn, and Mw respectively) with irradiation dose are given in Figure 6 and 7, respectively. As can be seen from these figures, all average molecular weights decreased rapidly up to 20 kGy.

Rapid decrease in $\overline{M}_n$ and $\overline{M}_w$ clearly indicated that the only mode of action of radiation on sodium alginate was degradation. For the determination of the G(S) values, $1/\overline{M}_n$ was plotted against dose for all samples (Figure 8). Then, G(s) values were calculated by using the intercepts. The calculated

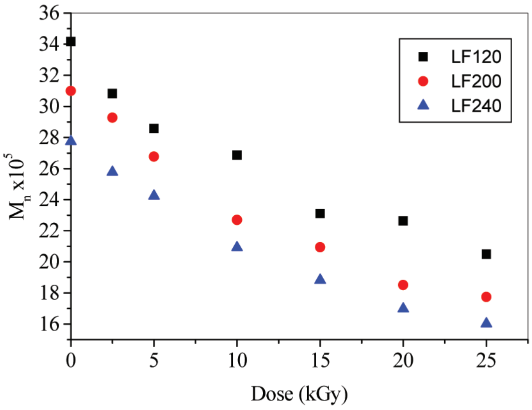

Figure 6. Change in the number average molecular weight ($\overline{M}_n$) of NaAlgs with dose.

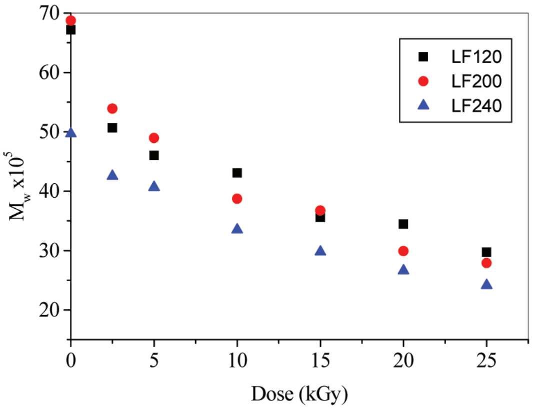

Figure 7. Change in the weight average molecular weight ($\overline{M}_w$) of NaAlgs with dose.

G(s) values were 0.073 ± 0.009, 0.100 ± 0.005, 0.1088 ± 0.003 μmol/J for LF120, LF200, and LF240 NaAlg, respectively. It was concluded that G(S) values were dependent on the structure (guluronic acids(G) and mannuronic acid(M) ratio) of the sample and followed the order LF240 > LF200 > LF120 or 70/30 < 50/50 < 45/55, G/M ratio.

When the chemical structures of NaAlgs were examined it was seen that the properties of NaAlg varied widely depending on the composition of the alginate molecule (i.e., the ratio of mannuronic to guluronic acids, the frequency and size of guluronic acid blocks, the molecular weight of the polymer), and the concentrations of alginate and cations at the time of gelation. It could be concluded that the G(S) value increased with a decrease in the guluronic acids to mannuronic acid ratio. This increase was attributed to the decrease of radical-radical recombination reactions due to the decrease of stiff and extended nature of alginate chains. It is well known that the diaxial linkage in G-blocks results in a large, hindered rotation around the glycosidic linkage, which may account for the stiff and extended nature of alginate chains [36].

The modified Jellinek equation [30] was used by Şen et al [14] in the determination of degradation rate. Degradation rate constants for NaAlgs were determined by using the curves $(1/\overline{M}_n)-(1/\overline{M}_{n_o})$ versus dose. The determined degradation rate constants for NaAlgs are given in Table 2. They followed the order LF240 > LF200 > LF120. These results clearly indicated that degradation rate was also dependent on the G/M ratio for these initial molecular weights.

Table 2. Degradation Rate Constants of NaAlgs.

Polymer	G/M	k(kGy^{-1})
LF120	70/30	4.27x10^{-10} ± 3.2x10^{-11}
LF200	50/50	5.86x10^{-10} ± 3.0x10^{-11}
LF240	45/55	6.30x10^{-10} ± 2.0x10^{-11}

In their study, change in viscosity with irradiation at different polymer concentrations and shear rates was investigated for all NaAlg samples. A representative figure for the change of viscosity with shear rate for the unirradiated, and the 2.5 and 5.0 kGy-irradiated LF120 NaAlg is given in Figure 9.

Shear rate versus shear stress, and shear rate versus viscosity curves became linear at an irradiation dose of approximately 2.5 kGy for LF120 NaAlg. Same behaviour was also observed for the other NaAlgs. Linearity of these plots indicated that the samples showed the Newtonian fluid properties. We could conclude that NaAlg lost the pseudoplastic fluid behaviour, and that the flow behaviour change from non-Newtonian to Newtonian even upon irradiation at very small doses.

Viscosimetric studies performed in different polymers concentrations and at different shear

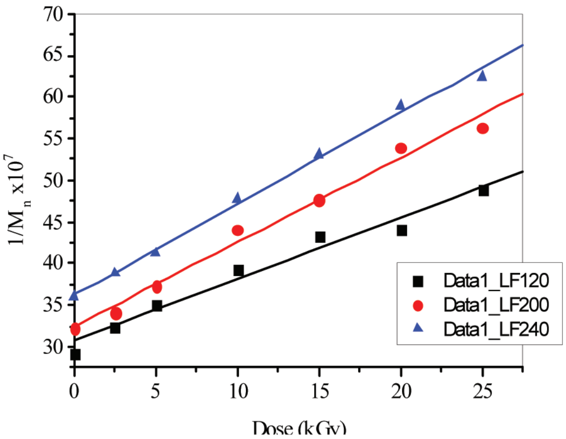

Figure 8. Plot of $1/\overline{M}_n$ versus dose for the determination of the G(S) values of NaAlgs.

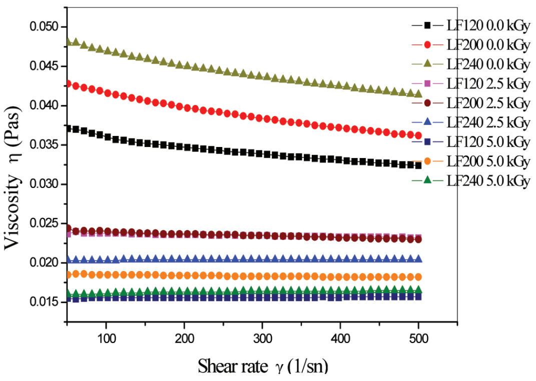

Figure 9. Change in the viscosity with shear rate for LF120 NaAlg irradiated at the indicated doses.

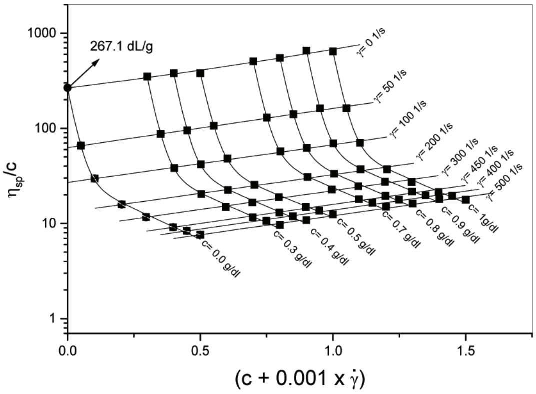

Figure 10. A plot for the determination of the limiting viscosity number of LF120 NaAlg for zero shear rate and zero concentration.

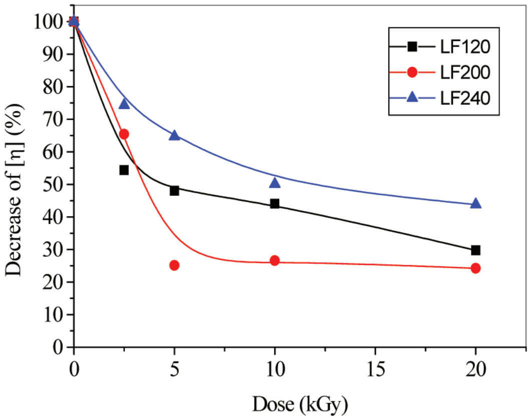

Figure 11. Decrease percentage in the limiting viscosity number for LF120 NaAlg with dose.

rates clearly indicated that the change in specific viscosity of NaAlg solutions depended on the shear rate and concentration of the solution. For the determination of limiting viscosity number of NaAlgs for zero shear rate and concentration, the rheological data were reanalyzed, and the η_{sp}/c values were plotted versus (c + 0.001 x $\dot{\gamma}$). The representative curves for the determination of [η] are given Figure 10. Similar curves were obtained for the other NaAlgs. Decrease percentage in [η] with irradiation is given in Figure 11. As can be seen in this figure, the decrease in viscosity followed the order LF200 > LF120 > LF240. These results clearly indicated not only that the rheological properties of the irradiated and molecular weight-reduced alginates were only controlled by G/M ratio, but also that the frequency and size of the guluronic acid blocks were important parameters. Despite the lower molecular weight and lower G/M ratio, the slower decrease in [η] value for LF240 with irradiation was due probably to the presence of more GG blocks in the main chain. Experimental viscosimetric data of alginate solutions indicated that the stiffness of the chain blocks increased in the order MC<MM<GG [36].

End of this study the authors conclude that as the guluronic acid to mannuronic acid ratio decreased, the effect of irradiation on the molecular weight and rheological properties of the sample became more pronounced and G/M ratio was one of the factors affecting chain scission yield of solid state irradiated NaAlg. All NaAlg samples showed a pseudo plastic behavior up to a certain dose, and Newtonian flow behavior above that dose.

In recent years studies are focused on the degradation of natural polymers in accelerated conditions by using additional OH radical generating systems such as hydrogen peroxide [37-38], ammonium per-sulfate [39] and nitrous oxide [40] in order to reduce irradiation dose for large scale production. OH-radical-induced chain scission of chitosan in the absence and presence of dioxygen are explained in details by Ulanski and Sonntag [41].

Şen et al. [15] investigated the effect of water and H_2O_2 on the radiation induced degradation of NaAlgs having different G/M ratios in 2% aqueous solutions and H_2O_2 containing solutions by irradiating at various doses (2.5, 5, and 10 kGy) using a Gamma cell 220 type ^{60}Co-gamma irradiator at room temperature in air. Dose rate was 30 Gy/h. For aqueous solution irradiations, NaAlg firstly dried in vacuum oven and then dissolved in pure water by stirring for 24 h. For the irradiation in H_2O_2 solution the proper amount of H_2O_2 was added to polymer solution. The concentration of H_2O_2 in solution is 2%.

For the investigation of the effect of gamma rays on the molecular weight of NaAlgs, their $\bar{M}_w$ and $\bar{M}_n$ values were evaluated using SEC.

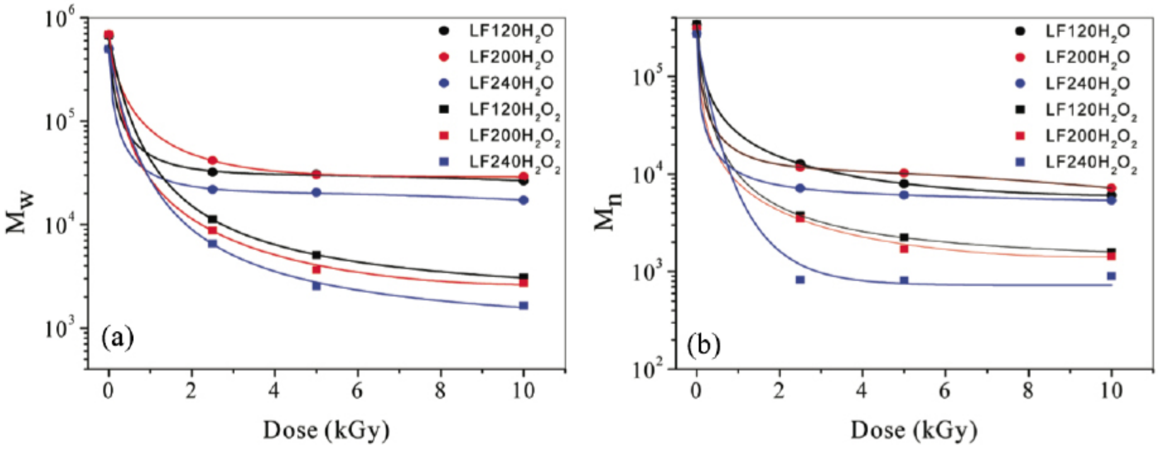

Figure 12. Change in the (a) weight and (b) number average molecular molecular weight ($\bar{M}_w$) of NaAlgs with dose in aqueous solution with and without H_2O_2.

Unimodal chromatograms were obtained for all NaAlg samples. As the irradiation dose increased, the SEC chromatogram of the NaAlg sample shifted to higher retention volumes indicating the molecular weight of the sample was decreased with irradiation. Changes in the weight and number average molecular weights ($\bar{M}_w$ and $\bar{M}_n$ respectively) with irradiation dose are given in Figure 12.

As can be seen from these figures, both average molecular weights decreased rapidly up to 2 kGy and almost constant after this dose value. The figure also indicates that H_2O_2 shows a synergistic effect on the degradation of NaAlg. The G/M is also an important factor controlling this synergistic effect. Better understanding the effect of irradiation media on the accelerated degradation of NaAlg, variation of Mw values of dry irradiated LF240NaAlg was compared with aqueous solution data in Figure 13.

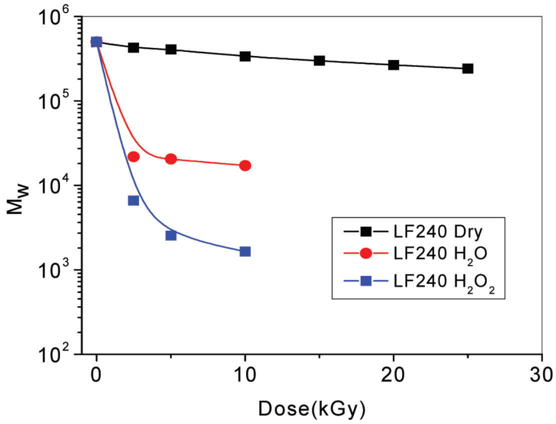

Figure 13. Variation of $\bar{M}_w$ values of LG240 NaAlg with dose in dry state and in aqueous solution with and without H_2O_2.

The synergistic effect of H_2O and H_2O_2 was also analyzed with chain scission yield G(S) value. The G-value, equal to mmol of events per J of energy absorbed, has been customarily used to measure radiation chemical yield.

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

The change in weight ($\bar{M}_w$) and number ($\bar{M}_n$) average molecular weights with dose for aqueous polymer solutions are given by the relations shown below:

$$G(S)-G(X)=\frac{c}{Dd}\left(\frac{1}{\bar{M}_{n_D}}-\frac{1}{\bar{M}_{n_0}}\right) \qquad (4)$$

$$G(S)-4G(X)=\frac{2c}{Dd}\left(\frac{1}{\bar{M}_{w_D}}-\frac{1}{\bar{M}_{w_0}}\right) \qquad (5)$$

Where c is the concentration of the polymer in solution (g/dm^3); D is the absorbed dose (Gy); d is the solution density (kg/dm^3), and the subscripts D and 0 refer to the respective quantities of the irradiated and unirradiated samples, respectively. The equations above are valid for polymers with initial most probable molecular weight

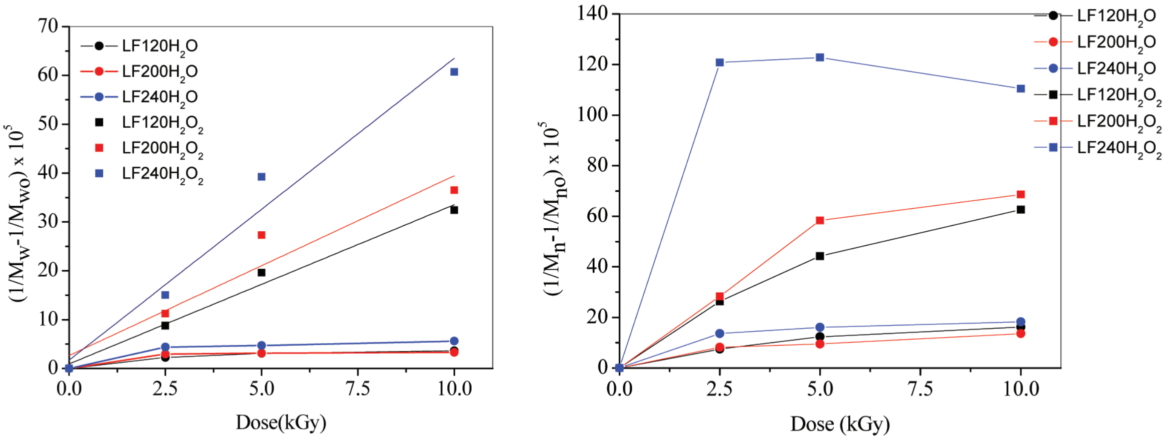

Figure 14. Variation of (a) $1/\overline{M}_w$ - $1/\overline{M}_{w_o}$ and (b) $1/\overline{M}_n$ - $1/\overline{M}_{n_o}$ values of LG240 NaAlg with dose

distribution and degree of polydispersity $\overline{M}_{w_o}/\overline{M}_{n_o}= 2$ [29]. If scission occurs only, then either Equation 4 or 5 alone can be used to calculate G(S) [42, 11]. When both crosslinking and scission occur, G(S) and G(X) can be obtained from the combination of the two equations provided that the initial molecular weight distribution is the most probable.

If scission is the only mode of action of radiation then the radiation-chemical yield of degradation (scission) G(S) (mol/J) is determined from the following equation:

$$G(S)= \frac{c}{Dd}\left(\frac{1}{\overline{M}_{n_D}} - \frac{1}{\overline{M}_{n_o}}\right) \qquad (6)$$

As it has been indicated above, in order to obtain quantitative information on chain scission yields, $1/\overline{M}_n$ and $1/\overline{M}_w$ vs. dose diagrams can be constructed according to Equations. 4 and 5 When this is done, Figures 14 (a) and (b) are obtained for $1/\overline{M}_w$ and $1/\overline{M}_n$ vs. dose.

From the overall slope of the linear parts of the curves (0 - 2.5 kGy) Şen et al have found that only mode of action of radiation is chain scission. Although it is possible to calculate a value for G(S) from the overall slope of the linear parts of the curves in this Figure, the authors have preferred to calculate individual values of G(S) as a function of dose by using Equation 4. The effects of irradiation media and dose on the G(S) value different G/M having NaAlgs are given in Table 3. As can be seen from table the yield is the lowest for dry irradiations γ/H_2O_2 irradiations and adding of H_2O and H_2O_2 degradation becomes more and more pronounced and G(S) values show an increase. The effect of NaAlg type or the G/M on the radiation induced degradation yields in aqueous solution irradiations was also examined. As can be seen from Figure 15 not only in dry irradiations also in aqueous solution irradiations the G/M ratio is an important factor controlling the degradation rate of sodium alginate. We conclude that chain scission yield (G(S)) values were dependent on the structure (guluronic acids (G) and mannuronic acid (M) ratio) of the sample and followed the order LF240 > LF200 > LF120 or 70/30 < 50/50 < 45/55, G/M similar as dry state .

Table 3. Degradation yield of NaAlgs irradiated with gamma rays in dry form (γ/dry) aqueous solution (γ/H_2O) and hydrogen peroxide solution (γ/H_2O_2).

G(s) value of sodium alginate (μmol/J)									
Irradiation mode	LF120			LF200			LF240		
	2.5 kGy	5.0 kGy	10 kGy	2.5 kGy	5.0 kGy	10 kGy	2.5 kGy	5.0 kGy	10 kGy
γ/dry	0.127	0.115	0.102	0.196	0.162	0.148	0.382	0.240	0.186
γ/H_2O	0.903	0.618	0.363	1.180	0.628	0.328	1.751	0.939	0.562
γ/H_2O_2	3.498	3.924	3.240	4.494	3.924	3.241	6.011	7.849	6.070

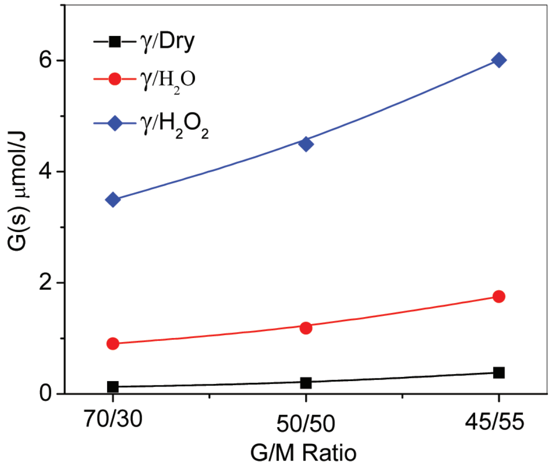

Figure 15. The effect of G/M ratio on the radiation induced degradation yields in aqueous solution irradiations. Irradiation dose is 2.5 kGy.

Effect of degree of deacetylation (DD) on the radiation induced degradation of chitosan

Chitin is one of the most abundant biodegradable natural polymers, after cellulose, in the world. Chitosan is produced commercially by deacetylation of chitin, which is a structural element in crabs, shrimp, and cell walls of fungi. The degree of deacetylation (DD), which determines the content of free amino groups in polysaccharides, can be employed to differentiate between chitin and chitosan. It is very well known that the degree of deacetylation is one of the most important chemical characteristics, which could influence the performance of chitosan in many of its applications [43].

In the more recent study, the effects of the DD of chitosans, which have a molecular weight, M_w ~ 330 kDa, and various DDs (78, 80, 88.6, and 97.4 %), on their radiation stability were investigated [44]. The chitosan samples were irradiated with gamma rays in air at ambient temperature in the solid state at doses ranging between 0-35 kGy, employing a low dose rate (3 Gy/h). The DD of the unirradiated or irradiated chitosans were determined by ^{1}H-NMR spectroscopy; and the degradation was monitored in detail by a careful Size Exclusion Chromatographic (SEC) and viscosimetric analyses of their respective molecular weights before and after the irradiation. The Charlesby-Pinner equation [29] was used to determine the radiation-chemical yields, G(S). It was found that the G(S) values increased with the DD value of chitosan at every absorbed dose within the dose range of 0-35 kGy.

From the results of this study, changes in the number average molecular weight (Mn) with irradiation dose are given in Figure 16. For the determination of the G(S) values, $(1/\overline{M}_n)$-$(1/\overline{M}_{n_0})$ was plotted against dose for all samples (Figure 17). Then, G(s) values were calculated by using the intercepts. The calculated G(s) values were 1.36, 1.37, 1.62 and 2.07µmol/J for 78, 80, 88.6, and 97.4 % deacetylatated chitosan respectively. The change in the scission yield and % reduction of limiting viscosity number (Figure 18) was attributed to the change in the coiled and extended nature of the chitosan chains that is a result of a change in the DD [44].

It is known that the extent of the coiling character of chitosan inversely proportional to its DD. It was concluded that, the high degree of coiling in the chitosan chains could result in a more compact structure that might enhance the radical-radical combinations on the chains, which would thus lower the rate of degradation and hence reduce the G(S) values.

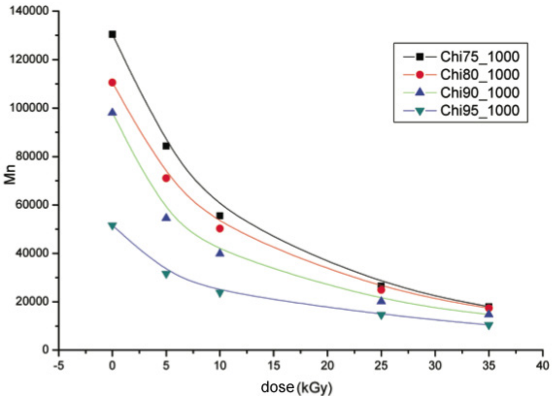

Figure 16. Change in the number average molecular weight ($\overline{M}_n$) of chitosan with dose.

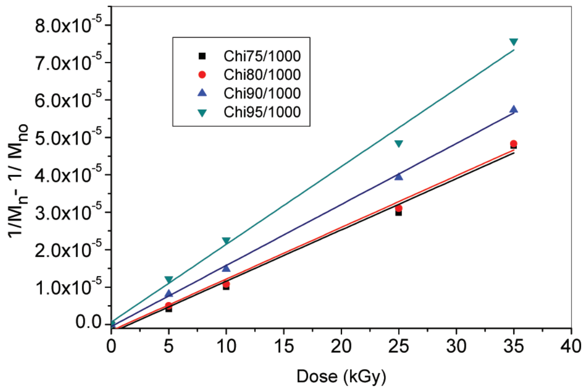

Figure 17. Variation of 1/$\overline{M}_n$ - 1/$\overline{M}_{n_o}$ values of chitosans with dose.

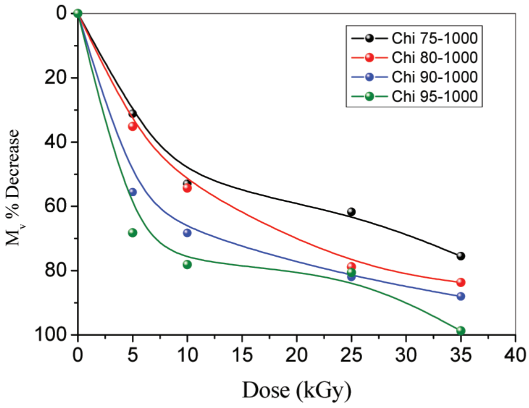

Figure 18. % decrease of viscosity average molecular weight of chitosans with dose

Conclusion

End of the research studies summarized in this review it has been proved that the structural one of the important parameter the radiation stability of parameters of polysaccharides. As the original molecular weight increased, effect of irradiation on the molecular weight and rheological properties of the galactomannans became more pronounced. It can be concluded that the mannose-to-galactose ratio (M/G) is not a factor affecting chain scission yield of galactomannans but the initial molecular weight is more important in affecting degradation rate of galactomannans under gamma rays. Galactomannan samples show a pseudo plastic behavior until a certain dose for and then they show Newtonian flow and loose their gelling properties.

When the effect of irradiation on the NaAlg samples was determined to be dependent on the chemical structure of the sample it has been observed that as the guluronic acid to mannuronic acid ratio decreased, the effect of irradiation on the molecular weight and rheological properties of the sample became more pronounced. It could be concluded that the guluronic acids to mannuronic acid (G/M) ratio was one of the factors affecting chain scission yield of NaAlg. All NaAlg samples showed a pseudo plastic behavior up to a certain dose, and a Newtonian flow behavior above that dose.

It has been found that degree of deacetylation (DD) is one of the critical parameters for the radiation stability of chitosan. As the DD ratio increased, the effect of irradiation on the molecular weight and rheological properties of the samples became more pronounced. It could hence be concluded that the DD ratio was one of the factors affecting chain scission yield G(S) of chitosan, and that the crystallinity of the chitosan chains could control its radiation stability.

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