

CHANGE IN GELLATION TIME OF SODIUM ALGINATE BIOPOLYMER HYDROGELS WITH CHANGE OF DOSE OF GAMMA IRRADIATION

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Abstract: Gamma irradiation induces many changes in the polymers and with that most of the properties of polymer gels. In this research we observed changes in gellation time of sodium alginate with changes in absorbed dose of gamma irradiation by measuring gel's viscosity from the start of gellation (activation of the gel forming component) to the end of gellation (maximum viscosity). Prior to gellation, the sodium alginate powder samples were gamma irradiated by exposing it to five different absorbing doses (nonirradiated, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy). We used sodium alginate with \bar{M}_w of $670 \cdot 10^3$ g/mol and G/M ratio of 70/30. CaCO_3 served as a source of Ca^{2+} ions for ionic (physical) cross-linking of the alginate and GDL as a weak acid for activation of Ca^{2+} ions. We found that the gellation time is in linear proportion to the absorbed dose of gamma irradiation of the sodium alginate polymer.

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1. INTRODUCTION

γ -Rays, with its high energy, impact and cut the polymer chains. Depending from the radiation flux and time and from there the absorbed dose there can be two results. In the first case when we have low dose the polymer chains cut and reconnect with a gellation effect on the polymer. In the second case when we have higher dose the polymer chains are cut in many places and this process is not followed with reconnection that leads to degradation of the gel. Splicing of the chain and degradation is followed with decrease of the molar weight of the polymer and with that a change in the mechanical and bioadhesive properties [1-3]. Here we used low doses of up to 10kGy and through compressibility tests we followed the degradation of the polymer gels. [4,5]. The average molecular weight between crosslink points in the gel M_c is connected to the number of crosslink points in unit volume. So if a γ quant enters this volume and cuts one covalent bond in the same time it can come to formation of two new crosslink

points increasing its number or a connection of two free chains reducing the number of crosslink points. In this way through the connection of M_c with the density of gel and elastic modulus we can follow the interaction of γ -rays with the gel network pic. 1.

Alginate is natural occurring polysaccharide found in substantial amounts in brown seaweeds. They are unbranched binary co-polymers of (1–4)-linked residues of b-D-mannuronic acid (M) and a-L guluronic acids (G). Alginic acid and its water-soluble sodium salt have a great ability to give highly viscous solutions even at moderate concentrations. 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 [6]. 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 and the molecular weight of the polymer [7,8].

Currently Ca^{2+} is preferred to crosslink alginate for biomedical applications because of the mild reaction conditions compared for example to the cellular toxicity of both Ba^{2+} and Sr^{2+} [9,10]. Two methods of gellation have been extensively described and used to create alginate hydrogels: diffusion gelling and in-situ gelling. Diffusion gelling is an ideal approach that is widely used for rapidly encapsulating cells and substances in microspheres of alginate used for controlled released methods where polymer gels swell in a medium in order to release a given substance. In this method calcium ions diffuse through the liquid alginate boundary, cross-linking alginate strands as the ions move through the volume of the alginate solutions. However, cross-links are not uniformly distributed throughout the gel that has a great influence on the properties of the gel including its swelling time. [11,12] . On the other hand, in recent years there has been a very big interest in the preparation of homogeneous alginate gels in different forms by using in-situ gelling methods. In this method $CaCO_3$ is mixed with alginate to create a homogeneous mixture. D-Glucono-d-lactone (GDL) is added to acidify the solution and release calcium ions, making them available for cross-linking. The resultant hydrogel has a uniform distribution of cross-links [13].

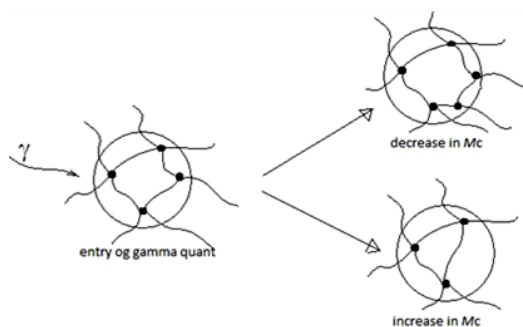


Fig. 1: Possible outcome after entry of gamma quant .

In this study we observe the change of gellation time with the change of dose of gamma radiation within different types of alginate. NaAlg powder samples were irradiated with gamma rays in air at ambient temperature in the solid state at low dose rates.

2. MATERIALS AND METHODS

Sodium alginate samples were obtained from FCM Biopolymers Company, Norway and used as received. The initial weight-averaged molecular weight of NaAlg type LF120M is \overline{M}_w of $670 \cdot 10^3$ g/mol, and the guluronic to mannuronic acid residues G/M is 70/30. Calcium carbonate and D-glucono- δ -lactone (GDL) were obtained from Aldrich. The polymer powder samples were placed in tightly closed cylindrical containers, and irradiated at the required doses of 2.5 kGy, 5 kGy, 10 kGy and 15 kGy in a Gammacell 220 type 60 Co-gamma irradiator at room temperature in air.

2.1 Preparation of Alginate Gels

A CaCO_3 -GDL system was used to achieve activated controlled gellation. Calcium carbonate (CaCO_3) was used as a source of calcium ions to initiate gellation and GDL was used as a weak acid for the activation of calcium ions from the carbonate. A molar ratio of calcium ion to GDL of 0.36 was used in order to secure preparation of an uniform gels from 1.5% sodium alginate solution as follows: 0.105g of sodium alginate was dissolved in 7 ml of deionized water and 0.0158 g CaCO_3 was put into the sodium alginate solution and the mixture was vortexed for 60 seconds. 0.056 g of GDL was dissolved in 0.02 mL of deionized water and added into alginate solution immediately and vortexed for 45 seconds and then put to rest. Through the same method calcium alginate activated solutions were prepared from irradiated sodium alginates [14].

2.2 Viscosity test equipment

After activation the solution is put in the cylindrical part of the test equipment. Then a type SC4-21 spindle is inserted and set to rotate at speed of 50 rpm. Temperature of the measurement was 25 °C. Sheer rate of the viscosity testings was 46.50 s^{-1} . During measurements the % torque changes from starting value up to max. of 105% when the motor of the instruments stops to prevent damage to the instrument. The tube and spindle are then cleaned and prepared for the next solution. It is noted that solutions are activated immediately before the viscosity test.

3. RESULTS AND DISCUSSION

Here we give the results for the gellation time for alginate irradiated with different gamma irradiation doses.

From fig.2 we get overall idea for the change in gellation time of the alginate with constant concentration and cross-link ratio but with different dose of irradiation. Starting from

fig.3 to fig.7 we give separate graphs for each dose with a logarithmic fit $y = (A_1 - A_2) / (1 + (x/x_0)^p) + A_2$ that gives us great extrapolation curve to find the final viscosity and gellation time.

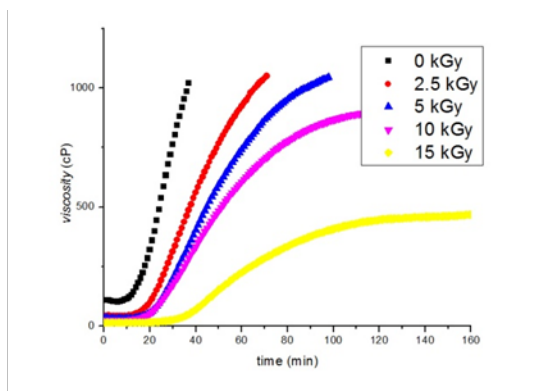


Fig. 2: Overall change in gellation time for alginates

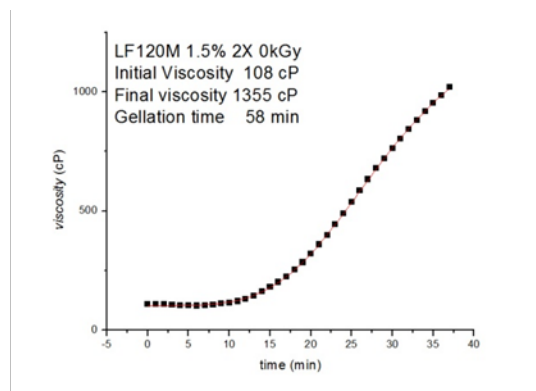


Fig. 3: Gellation curve for alginate type LF120M at 0 kGy.

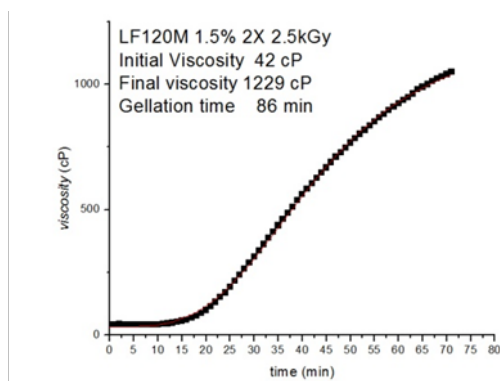


Fig. 4: Gellation curve for alginate type LF120M at 2.5kG.

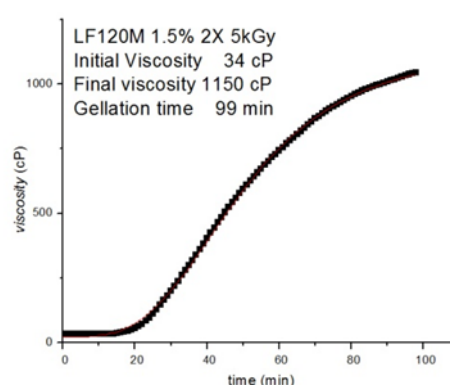


Fig. 5: Gellation curve for alginate type LF120M 5 kGy.

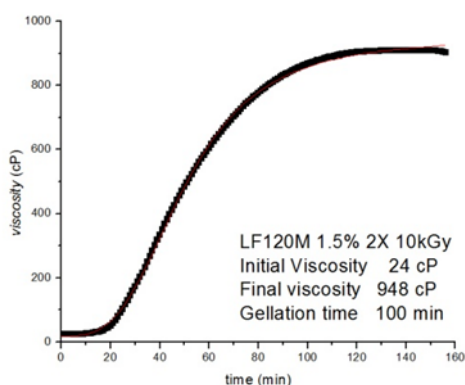


Fig. 6: Gellation curve for alginate type LF120M at 10 kGy.

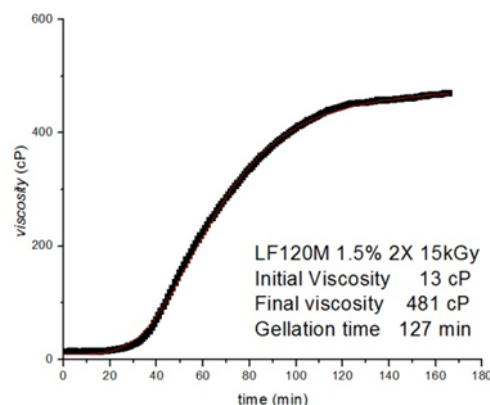


Fig. 7: Gellation curve for alginate type LF120M at 15 kGy.

In the following table we summarize the results.

Table 1: Viscosity results.

Irradiation (kGy)	Initial Viscosity (cP)	Final Viscosity (cP)	Gellation time (min)
0	108	1355	58
2.5	42	1229	86
5	34	1150	99
10	24	948	100
15	13	481	127

From a linear fit of the results shown in Table 1 we can see that the final viscosity decreases linearly with increase of the irradiation dose (Fig.8). The results in table 1 clearly show that gamma radiation has a degrading effect on the polymer. Because the gellation time is connected to the molecular weight or simply the length of the chains we see that with the increase of the dose the polymer degrades and with it the time it takes for the chains to form a gel network increases.

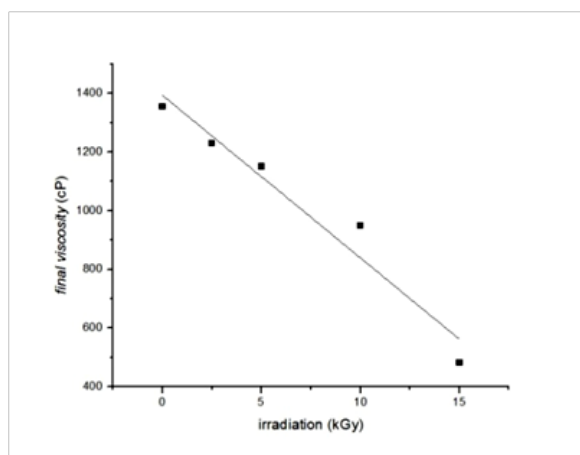


Fig. 8: Linear fit of the decrease in the final viscosity.

4. CONCLUSION

In this study we confirm that irradiation has a degrading effect on the structure of alginates and that increase in gellation time is linearly correlated to the absorbed dose of gamma irradiation. In further research that we are going to follow it is of great importance to determine the molecular weight of the irradiated alginates and correlate the molecular weight to the final viscosity. In this way if we know the initial molecular weight of nonirradiated alginate sample we can use gellation time experiment as another method to determine the molecular weight of the irradiated alginates at any doses.

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