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Effect of Cross-linking Time on Sodium Alginate Based Blend Films as a Supporter of Bordeaux Mixture

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ABSTRACT

Blend films based on sodium alginate (SA) are synthesized and the use of these films as a supporter for Bordeaux mixture to adhere the crops for longer time and sustained release of active ingredient were studied. An aqueous solution of Sodium alginate was prepared and the obtained solution was added to bordeaux mixture of fixed compositions. Alginate solution is cross-linked by the multivalent cations present in bordeaux mixture and forms films. Blends based on sodium alginate with gelatin (SAGN) and sodium alginate with guar gum(SAGM) were synthesised. The thickening and cross linking action of these films were controlled by varying the cross linking time. The films were dried at 50^{o}C in an oven and kept in different buffer solutions for swelling studies. From the swelling data, rate and kinetics of swelling were studied and swelling parameters were tabulated. The swelling parameters showed that the various bordeaux mixture cross-linked films were stable and they can absorb sufficient quantity of water and may prevent leaching out of active ingredients on rough weathers. Also the cross-linked polymer film may serve in increasing life and sustained release of active ingredients.

Key words: Blends, Bordeaux mixture, ionic cross linking, pH sensitivity, sustained release

1. INTRODUCTION

Hydrogels are three dimensional networks of hydrophilic polymers obtained by physical or chemical cross linking of the polymer chains. They possess the ability to absorb large amount of water while retaining the three dimensional structure and find extensive use in medical, pharmaceutical, agricultural and industrial fields[1-3]. "Stimuli responsive hydrogels" refers to a special class of hydrogels which exhibit dramatic changes in their physical or chemical behavior in response to slight variations in external conditions such as temperature, ionic strength or pH of the medium etc. Intensive studies are being carried out on the development of such hydrogel materials, especially for biomedical and pharmaceutical applications [4-6]. Hydrogels have been extensively used in agriculture as a moisture conditioner for soil and controlled release of active ingredients like fertilizer and micro-nutrients. Cross linking of polymer matrix with selected polyvalent cations can improve rheology of the matrix, controlled release of the active ingredient and controlled release of bio compatible ions if used[7,8]. Again by incorporating spherical eco-friendly nano particle allows the modification of the physical properties of polymers as well as the implementation of new features in the polymer matrix[9,10].

2.EXPERIMENTAL PROCEDURE

2.1. Materials

Sodium alginate, gelatin, guar gum, calcium chloride, copper sulphate, potassium hydrogen phthalate, potassium dihydrogen

orthophosphate, disodium hydrogen orthophosphate dihydrate and hydrochloric acid were obtained from S.D. Fine Chemicals (Mumbai, India). Doubly distilled water was used in the preparation of the films and for swelling studies.

2.2. Preparation of IPN Films

In the present study, the following method was used for the preparation of the films. 2% (w/v) aqueous solutions of Sodium Alginate (SA) were prepared by stirring at room temperature. The optimum amount of each solution was poured on a glass plate and cast into films of thickness ≈ 0.2mm by solvent evaporation at 60^{o}C. The dried films were removed and immersed in a 1% (w/v) solution of bordeax mixture. After specific time intervals, the crosslinked films were taken out and washed with distilled water to remove the adhering chemicals. The films thus obtained were dried at 40^{o}C under vacuum and stored. Later 2:1 w/w polymer blend films were prepared by mixing sodium alginate with gelatin and guar gum separately. These films were crosslinked with the same procedure as mentioned above with 1% (w/v) of solution of bordeaux mixture. The details of the preparation conditions and the codes used for the designation of the films are compiled in Table 1.

Table 1: Sample code and preparation conditions

Code	SA(%)	GN(%)	GG(%)	Conc.of Bordeaux mixture(%)	Time of crosslinking (min.)
SGG1	2	0	0	1	10
SGG2	2	0	0	1	30
SGG3	2	0	0	1	60
SGG4	2	1	0	1	10
SGG5	2	1	0	1	30
SGG6	2	1	0	1	60
SGG7	2	0	1	1	10
SGG8	2	0	1	1	30
SGG9	2	0	1	1	60

2.3. Swelling studies

Completely dried hydrogel samples were left to swell in a solution of pH 7 at constant temperature. The swollen gels were taken out at regular time intervals, wiped superficially with filter paper, weighed and placed in the same bath. The weighing was done using electronic balance. The measurements were continued until the constant weight was attained for each sample. The percentage of mass swelling (%S) were obtained by the expression[11].

$$\text{Swelling Percentage } (S\%) = \frac{Wt - Wo}{Wo} \times 100 \quad (1)$$

Where Wo and Wt are weights of dry and swollen gels respectively. Percentage equilibrium water content(%EWC),the amount of water a swollen gel can hold at equilibrium was calculated(26) using the following equation[12].

$$EWC(\%) = \frac{We - Wo}{We} \times 100 \quad (2)$$

Where We is the weight of gel at equilibrium. All the experiments were repeated in triplicate.

The diffusion is the ability of the penetrant to move among the polymer segments. Diffusion coefficient of pure SA and blend films were calculated using a short time approximation, which is valid only for first 60% of the swelling. In this method, to calculate the diffusion coefficient Wt/W∞ plots were made and from the slope of the lines diffusion coefficients of the films were calculated using the equation [13].

$$\frac{Wt}{W\infty} = \frac{4}{r}\sqrt{\frac{Dt}{\pi}} \quad (3)$$

Where ‘t’ is the time, ‘d’ is the initial thickness of the film, ‘D’ is the diffusion coefficient, ‘Wt’ is the solvent uptake of the sample at a time t and ‘W∞’ is the equilibrium mole percent uptake.

3.RESULTS AND DISCUSSIONS

3.1. Swelling studies of SA based blend fims

The percentage swelling data collected as a function of time in medium of pH.7.0 are displayed in Table 2. The data clearly indicates the influence of polymer composition and extent of crosslinking of the functional groups of the polymer chains. The nature of the percentage swelling versus time plot indicate that amount of water absorbed into the gel increases with at a faster rate in the beginning and after certain period, the rate slows down and the gels gradually reach their equilibrium swelling level.

3.1.1. Effect of Crosslinking Time

The swelling studies were carried out for SA, SAGN and SAGM gels at pH 7. For SA gels the percentage of swelling decreases from 382 to 204 with exposure time increases from 10 to 60 minutes. The same trends were observed for SAGN and SAGM gels films. For SAGN films the percentage of swelling decreases from 503 to 223 and for SAGM films 486 to 368. This trend is mainly due to the increase in the number of crosslinks in the gels with the increase in the time period of contact of the films with the bordeaux mixture medium. Higher the time of contact, lower is the swelling. With increase in the crosslinking nature of the network, the polymer chains are held tight, decreasing the hydrodynamic free volume available for accommodation of water molecules and thereby causing decrease in swelling. The details are given in table 2 and figures 1-3.

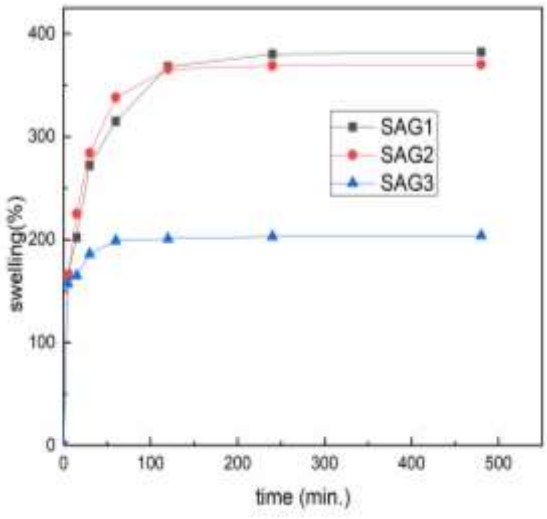

Fig. 1. Swelling % of SA Gels

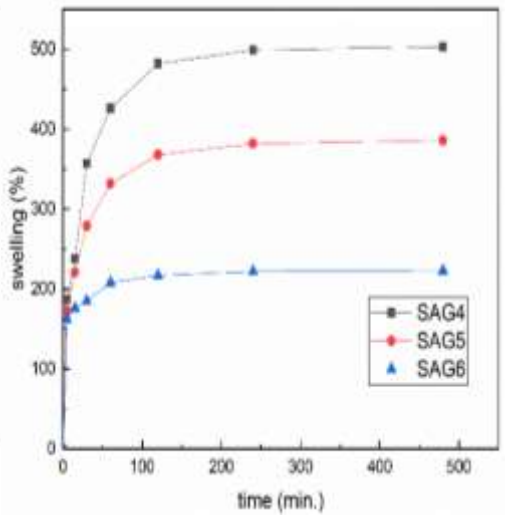

Fig.2. Swelling % of SAGN Gels

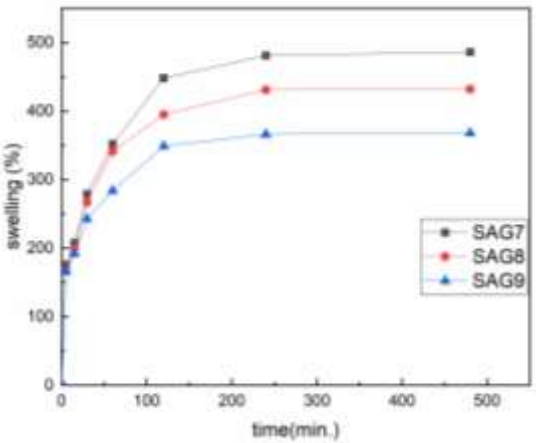

Fig. 3. Swelling % of SAGM Gels

3.2. Kinetics of swelling

The swelling data were fitted into the 't/S' vs 't' plot is displayed in fig.4-6. The initial rate of swelling 'Ri' and swelling rate constant 'k_s' for the gels were calculated from the intercept of the respective curves on the ordinate axis and theoretical equilibrium swelling 'S_{max}' from the corresponding slopes. The value of these parameters obtained for the gels are presented in Table 2.The linearity of the plot indicates that the swelling process follows second order kinetics. From the table, it is confirmed that the 'maximum equilibrium swelling ratio' values calculated theoretically from the slopes are in good agreement with the equilibrium swelling ratio determined experimentally by swelling measurements.

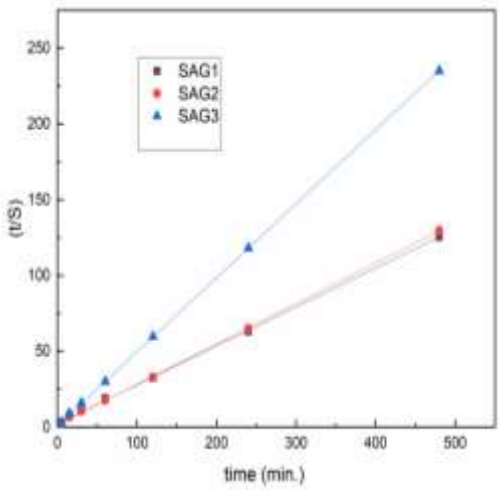

Fig. 4. Swelling rate curves of SA Gels

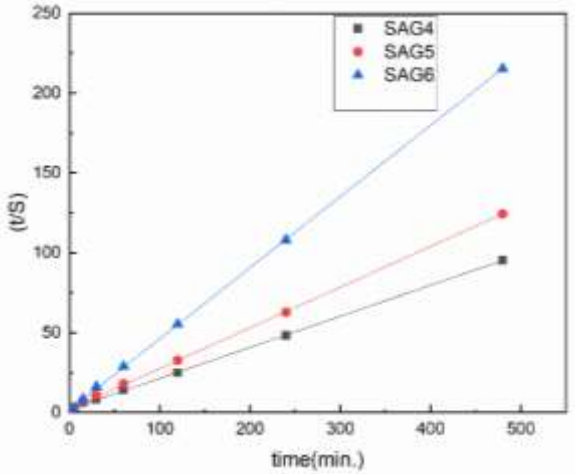

Fig. 5. Swelling rate curves of SAGN Gels

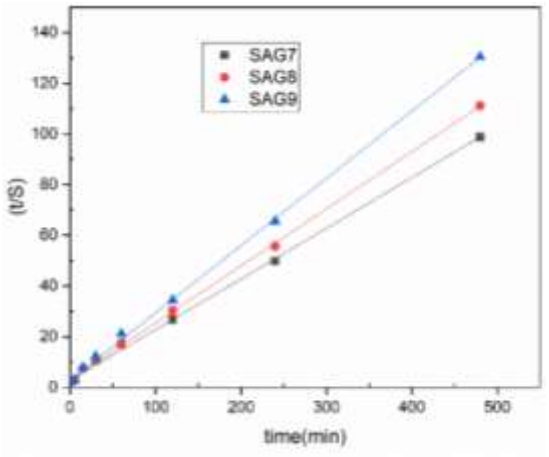

Fig. 6. Swelling rate curves of SAGM Gels

3.3. Mechanism of swelling

Swelling exponents('n') and swelling constants(K) were calculated from the slopes and intercepts of the lines of 'ln F' vs. 'ln t' plots (Fig. 7-9) and are listed in Table 2. The 'n' value varied in the range 0.25 to 0.37 in case of SA gels. The swelling exponent increases in the case of SAGM gels from 0.12 to 0.2. The 'n' values show no much variation in case of SA/gelatin gels. No much variation is observed for the values of swelling constant and it can be said that the mechanism of transport of matter into the composite system could be anomalous.

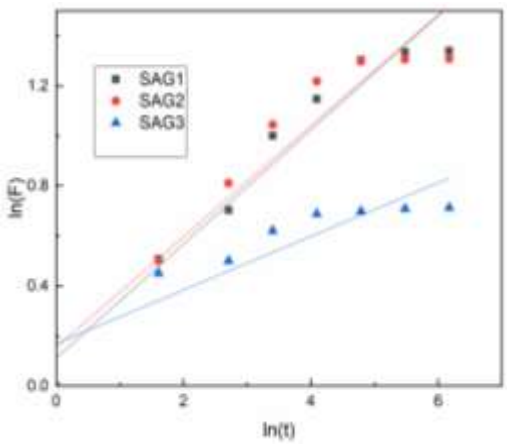

Fig.7. Swelling kinetic curves of SA Gels

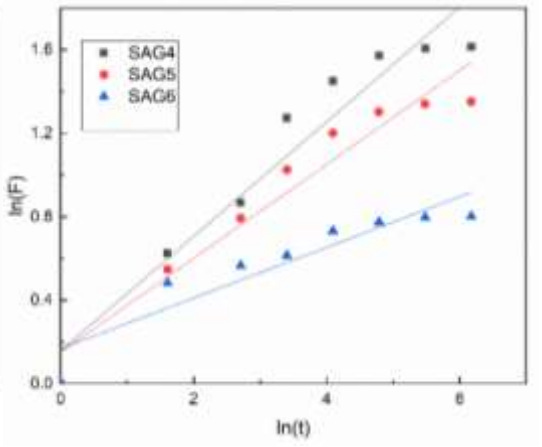

Fig.8. Swelling kinetic curves of SAGN Gels

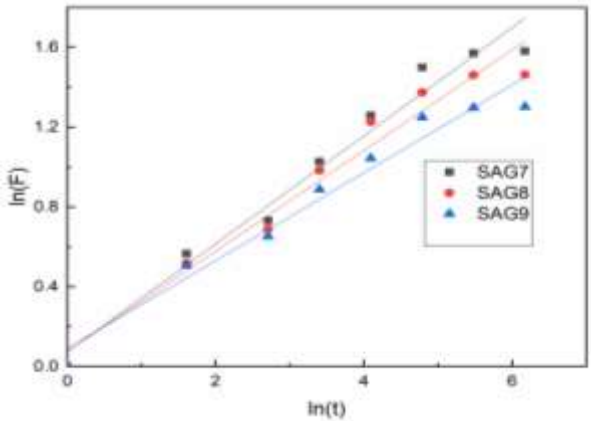

Fig.9, Swelling kinetic curves of SAGM Gels

3.4. Diffusion kinetics of water

With the swelling data, W_t/W_∞ vs $t^{1/2}$ plots were constructed for representative samples and the results are displayed in fig.10-12.The diffusion coefficients (D)were calculated from the slope of the lines and are listed in table 2. It was observed that the values of the diffusion coefficient of SA gels decreases form 7.074 $\times 10^{-4}$ cm^2 min^{-1} to 1.036 $\times 10^{-4}$ cm^2 min^{-1}. This may be due to an increase in extent of crosslinking. In SAGN & SAGM gels the D values decreases from 3.726 $\times 10^{-4}$ cm^2 min^{-1} to 0.925$\times 10^{-4}$ cm^2 min^{-1} and 8.675cm^2 min^{-1} to 2.906 cm^2 min^{-1} respectively. Here also when the gel becomes more and more crosslinked the compactness of the gels increase and thereby the value of diffusion coefficient decreases.

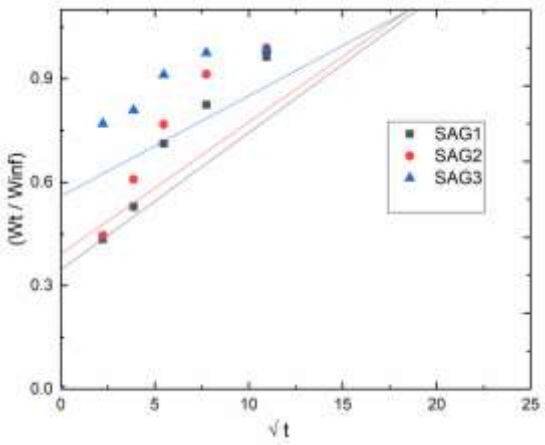

Fig.10. Swelling kinetic curves of SA Gels

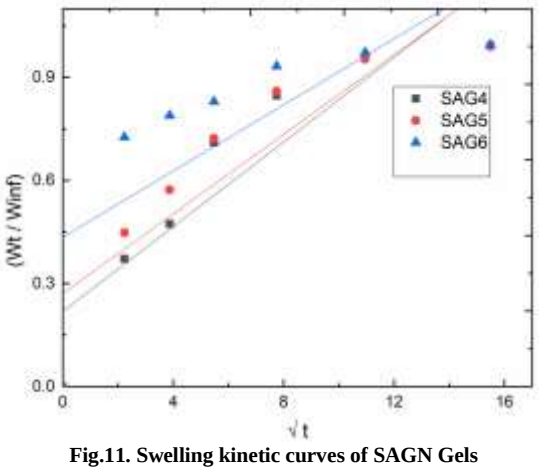

Fig.11. Swelling kinetic curves of SAGN Gels

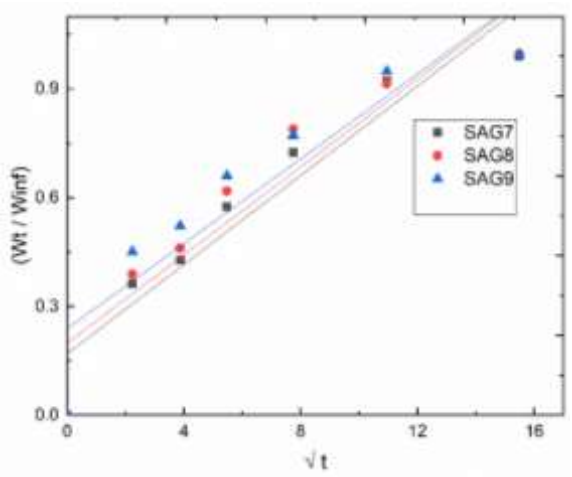

Fig.12. Swelling kinetic curves of SAGM Gels

Table 2. Some swelling parameters

Particulars	SAG1	SAG2	SAG3	SAG4	SAG5	SAG6	SAG7	SAG8	SAG9
Swelling percentage, S %	382	370	204	503	386	223	486	432	368
Equilibrium swelling, Seq %	390	375	205	514	392	224	499	444	376
Initial swelling rate, Ri	0.442	0.642	1.026	0.531	0.495	0.868	0.369	0.355	0.358
Swelling rate constant, $K_s \times 10^{-2}$	2.912	4.553	0.243	0.020	3.22	17.2	1.47	1.80	0.025
Swelling exponent, n	0.245	0.337	0.373	0.347	0.331	0.370	0.159	0.162	0.200
swelling constant, K	0.128	0.140	0.145	0.141	0.139	0.145	0.117	0.118	0.122
Diffusion coefficient, D $\times 10^{-4}$ cm^2 min^{-1}	7.070	4.082	1.036	3.276	1.038	0.925	8.675	3.081	2.906

CONCLUSION

In the present work blend films based on sodium alginate (SA) were synthesized by varying polymer compositions and crosslinking time. Blends based on sodium alginate with gelatin (SAGN) and sodium alginate with guar gum (SAGM) were also synthesised. The thickening and cross linking action of these films were controlled by varying the cross linking time. The films were dried at 50^{o}C in an oven and kept for swelling studies. Weight and stability of these films with time were noted at 10, 30 and 60 minutes. From the swelling data, rate and kinetics of swelling were studied and swelling parameters were tabulated. It was observed that for SA gels the percentage of swelling decreases from 382 to 204 with exposure time increases from 10 to 60 minutes. The same trends were observed for SAGN and SAGM gel films. For SAGN films the percentage of swelling decreases from 503 to 223 and for SAGM films 486 to 368. From diffusion experiments it was found that the diffusion is anomalous in nature. The swelling parameters showed that the various bordeaux mixture cross-linked films were stable and they can absorb sufficient quantity of water and may prevent leaching out of active ingredients on rough weathers.

Declaration by Authors

Ethical Approval: Not Applicable
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Conflict of Interest: The authors declare no conflict of interest.

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