



Kinetics, absorption and diffusion mechanism of crosslinked Chitosan Hydrogels

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Green polymers are extremely useful for various environmental applications. One such biopolymer is Chitosan. In this study, crosslinked and physical Chitosan hydrogels were synthesized. The swelling of disc-shaped hydrogels crosslinked using different concentrations of Glutaraldehyde were compared with physical film and bead shaped hydrogels. Best swelling of around 3000% was observed in case of square film shaped hydrogels but they lacked rigidity and dissolved in mild acids. In case of crosslinked hydrogels, as the crosslinker concentration increased, the hydrogels entrapped less water but gained better mechanical strength. Characterization of synthesized crosslinked hydrogels was carried out using FTIR, TGA and DSC. Equilibrium swelling results indicated more water absorption at acidic pH (2.5). Simultaneously, increase in temperature led to enhancement of swelling degree. The hydrogels trapped more water leading to increased swelling, in case of lower molar salt concentrations. Second order kinetics was followed due to stress relaxation of polymeric chain. Diffusion was found to be anomalous since exponent values lied between 0.5 and 1. Peleg's and Exponential association model were used to carry out absorption modeling. The data was found to fit the Peleg's absorption model. Degree of swelling is a major factor for deciding a hydrogels utility. Swelling ability, biocompatibility and availability of lone pairs of oxygen and nitrogen on the surface of CS makes it ideal for applications in drug delivery, controlled release of fertilizers and adsorption of environmental contaminants.

Keywords: Chitosan, Swelling kinetics, Peppas model, Peleg's and Exponential association model

1 Introduction

Hydrogels are 3-dimensional hydrophilic polymeric networks in which water acts as the dispersion medium¹. Superabsorbent polymers are the hydrogels, which show a high swelling percentage (>100) for water or other fluids^{2,3,4}. The hydrophilicity in these hydrogels/ superabsorbent polymers may be attributed to presence of groups such as hydroxyl (-OH), amidic (-CONH-), carboxylic (-COOH) and sulphonic (-SO₃H), which are polar in nature⁵. Hydrogels may be synthetic or natural polymer based hydrophilic networks. Some of the synthetic polymers used in hydrogel formation are acrylic acid, acrylamide, polyurethane and poly (ethylene glycol). Biopolymers used for synthesis of hydrogels are usually polysaccharides such as cellulose, dextran, starch and chitosan (CS)⁶.

In most of the commercial applications such as diapers, acrylate based hydrogels are employed that take several years to degrade. Therefore, superabsorbents with rapid biodegradability and less

toxicity are being researched upon for their utility in industrial and commercial applications⁷.

CS is a cationic biopolymer having chemical formula $\beta(1,4)$ -2-amino-2-D-glucose. It is a biopolymer obtained from processing of chitin and is known for its biocompatibility, biodegradability and abundance⁸. CS has hydrophilic functional groups and can be used for synthesizing hydrogels. The biggest challenge of working with CS is that it lacks mechanical strength as compared to synthetic polymers. For improving its mechanical strength and workability, it can be either blended with other polymers like acrylamide^{9,10} or crosslinked with agents such as glutaraldehyde and genipin¹¹.

Hydrogels are known for their high swelling ability and take several hours to achieve equilibrium or maximum absorption capacity. The applicability in areas such as drug delivery or as controlled release fertilizers depends on the rate and degree of swelling of hydrogel⁵. Most dried hydrogels take time to achieve equilibrium because the diffusion of water into the glassy framework is a slow process¹². Mathematical modeling of swelling is an important

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aspect for behavior and applicability of hydrogel under different environmental conditions. This has gained a lot of attention in recent years.

The kinetics of hydrogel swelling has been described through various mathematical models. The most commonly used is Fickian diffusion model that describes solvent distribution into the gel matrix during its swelling or collapsing¹³. As per this model, the swelling fraction tends to increase linearly with square root of time till a fraction of 0.4 and the swelling curve is never sigmoidal in shape till this range. The second model is the collective diffusion model that relates the stress gradient with the swelling and network expansion of the gel¹⁴. Both of these models fail to describe sigmoidal swelling curves resulting from large volume changes. Sigmoidal swelling curves often tend to describe the non-Fickian diffusion behavior. The Fickian diffusion describes the sigmoidal swelling behavior when the movement of gel surface is considered correctly¹⁵.

Scarce literature is available on the swelling properties and mathematical modeling of CS hydrogels and also on the comparison of degree of swelling for different hydrogel shapes. There has been a growing interest in the area of shape changing hydrogels in response to external stimuli¹⁶. Few reports are available in literature on crosslinking of CS with glutaraldehyde^{17,1,18,11}. The novelty in this synthesis is that the quantity of crosslinker involved is lower than that available in literature and different shapes of CS have been compared along with their swelling kinetics in a single manuscript. To the best of our knowledge, absorption modeling has not been carried out for crosslinked CS hydrogels.

Henceforth, we have attempted to synthesize CS hydrogels in the form of beads, discs and films and subsequently investigated swelling characteristics of synthesized hydrogels for its percent equilibrium swelling and diffusion coefficient. Further the order of kinetics was evaluated using two mathematical models, which were not attempted earlier for estimating swelling kinetics parameters of CS hydrogels namely Peleg's model and Exponential association equation model. Best-fitted model was also yielded from experimental data.

2 Materials and Methods

2.1 Materials

CS or Poly(beta-(1,4)-D-glucosamine) (Acros Organics, USA) with molecular weight 600000-

800000 Da (1526.464 g/mol) and degree of deacetylation 90-98%, glutaraldehyde 25% solution (Thomas Baker), acetic acid glacial (Fisher Scientific) were used as received. All the solutions were prepared using double distilled water. Wherever required, pH was adjusted using 0.1M HCl and 0.1M NaOH.

2.2 Methods

2.2.1 Synthesis of CS Hydrogels

Uncrosslinked CS beads

CS (1 g) was added to 10mL 1% (v/v) acetic acid dissolved in 50mL distilled water. The components were mixed vigorously using a magnetic stirrer till a uniform solution was obtained. After an hour, drops of CS and acetic acid mixture were added to 0.1N NaOH kept in another beaker. The NaOH solution acts as a precipitation bath for the formation of chitosan beads¹⁹. The beads formed were left for 1 hr. in NaOH for hardening. The beads were then taken out, washed and dried and then placed in different pH solutions for determining the swelling.

Uncrosslinked CS films

The same procedure was followed for the synthesis; the only difference being that instead of pouring the mixture as drops in NaOH precipitation bath, the mixture was poured uniformly over a petridish and was allowed to dry completely at room temperature. The beads form in a precipitation bath whereas spreading, drying and removing the layer can form the film. Once the film dried, a 2.5x2.5cm square was cut and placed in solutions of different pH to check the swelling.

Disc shaped crosslinked CS Hydrogels

CS was mixed in 10mL 1% (v/v) acetic acid and the solution was stirred in 100mL beaker^{20, 21}. Glutaraldehyde solution that acts as crosslinker was added before transferring the contents to test tubes and was thoroughly mixed for about 5-10 minutes till the solution turned slightly viscous. The total content was kept as 50 mL by adding remaining quantity of distilled water. The test tubes were retained at room temperature and hydrogel formation was observed within an hour. The tubes were broken and hydrogels were removed and cut in the form of equal sized cylindrical disks. The disks were thoroughly washed with water and kept for drying in oven at 35°C. The following compositions of hydrogel prepared along with their notations are stated in Table 1.

The synthesis mechanism between the carbonyl group of glutaraldehyde and amino groups of CS is

Table 1 — Notations and Composition of Hydrogels formed

Notation of Hydrogel formed	CS (g)	Glutaraldehyde (mL)	State of Hydrogel formation
CS ₁ Gl _{0.2}	1	0.2	Flaccid Hydrogel
CS ₁ Gl _{0.4}	1	0.4	Firm Hydrogel with a good texture
CS ₁ Gl _{0.6}	1	0.6	Highly viscous Hydrogel

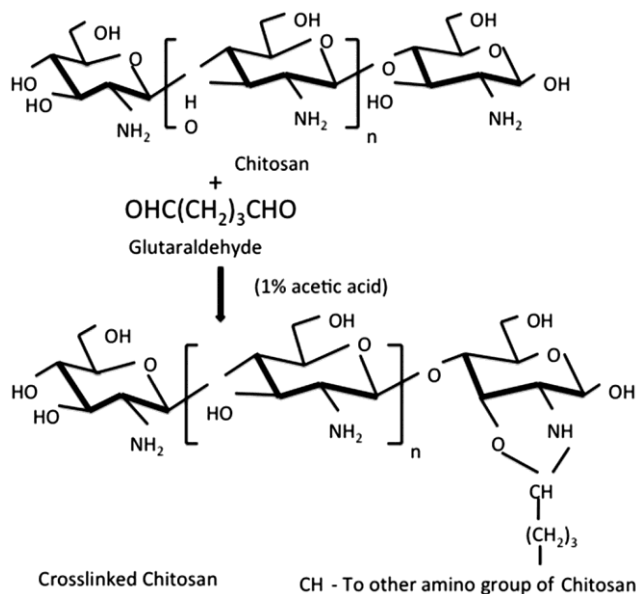


Fig. 1 — Mechanism of synthesis of crosslinked CS hydrogels

shown in Fig. 1. Due to the lone pair of electrons present on nitrogen part of amino group, there is a nucleophilic attack reaction by the carbonyl carbon of glutaraldehyde.

2.2.2 Swelling studies

Swelling ratio (SR)

Swelling ratio of the hydrogel was assessed using gravimetric measurement. The dried pellet form hydrogel sample was placed in a 100mL beaker filled with 50mL distilled water at 25°C. The swollen hydrogel was regularly taken out from the beaker at different time slots and wiped with a blotting sheet. Then it was weighed and kept back in the beaker²². The equation used for calculating SR was:

$$SR = \frac{\text{Weight of Swollen sample}}{\text{Weight of dry sample}} \quad \dots (1)$$

Equilibrium swelling (ES%)

The ES% of hydrogel was assessed by keeping disc shaped hydrogel in distilled water at different pH, temperatures and salt solutions²³. The equation used was:

$$ES\% = \frac{(W_{sw} - W_{dr})}{W_{dr}} * 100 \quad \dots (2)$$

where, W_{dr} is weight of dry hydrogel and W_{sw} is weight of swollen hydrogel.

Equilibrium water content (EWC)

In order to get the quantitative estimation of the amount of water absorbed by the hydrogel, EWC value is calculated using the equation:

$$EWC = \frac{(W_{sw} - W_{dr})}{W_{sw}} * 100 \quad \dots (3)$$

Swelling Kinetics

Order of Kinetics

The kinetic order and rate of swelling of CS hydrogels can be yielded through method prescribed by Druzynska, 2015²⁴.

First-order kinetics: The rate of swelling of hydrogel at any time (t) can be expressed as:

$$\frac{dS}{dt} = k_{1r}(S_{eq} - S) \quad \dots (4)$$

where, k_{1r} is the rate constant of first order kinetics.

Integrating Eq. 4 between the limits of $S=0$ to S at t from 0 to t ,

$$\ln \frac{S_{eq}}{(S_{eq} - S)} = k_{1r}t \quad \dots (5)$$

If the plot of $\ln(S_{eq}/(S_{eq}-S))$ against t gives a straight line and R^2 values approaching 1, the absorption by hydrogel shows first order kinetics.

Second-order kinetics: If the hydrogels tend to follow second order absorption kinetics^{25,1}, the equation can be stated as:

$$\frac{dS}{dt} = k_{2r}(S_{eq} - S)^2 \quad \dots (6)$$

On integrating Eq. 6 from $S=0$ to S and $t=0$ to t ,

$$S = \frac{k_{2r}S_{eq}^2t}{1+k_{2r}S_{eq}t} \quad \dots (7)$$

On rearranging,

$$\frac{t}{S} = \frac{1}{k_{2r}S_{eq}^2} + \frac{t}{S_{eq}} \quad \dots (8)$$

If the plot of t/S against t gives a straight line with R^2 values close to 1, hydrogel follows second order kinetics of absorption.

Diffusion mechanism

Fick's law is used for obtaining the description of diffusion of water in polymeric network with respect to different factors. Swelling kinetic parameters for

polymers can be obtained by theory given by Peppas et al., 2000²⁶.

$$F = \frac{S_t}{S_{eq}} = kt^n \quad \dots (9)$$

where, “F” represents the swelling fraction, “S_{eq}” is the swelling seen in hydrogel when equilibrium is achieved, “n” is a solvent based diffusion parameter, and k is the constant based on gel structure. Parameter “n” helps us in identifying the type of diffusion.

“n” values can be obtained from slope of ln F versus ln t graph by plotting the data till 60% solvent has entered the gel structure while “k” is obtained from intercept values¹².

As per the Fick’s second law of diffusion, for cylindrical hydrogels, the diffusion coefficient can be represented using the following equation:

$$D = \pi r^2 \left(\frac{k}{4}\right)^{\frac{1}{n}} \quad \dots (10)$$

where, ‘D’ represents the diffusion coefficient having S.I. unit m²s⁻¹ and ‘r’ represents the radius of the swollen hydrogels having S.I. unit ‘m’.

Absorption Kinetics Modeling

Water absorption has been studied and researched upon by many researchers. They have proposed some absorption models such as Peleg’s model²⁷ and Exponential association model²⁸.

Peleg’s empirical equation involving two parameters has been used for describing water absorption by grains/ material²⁹:

$$S = S_0 \pm \frac{t}{k_1 + k_2 t} \quad \dots (11)$$

where, S₀ is the initial swelling value when t = 0 (g/g)

S is the swelling value of hydrogel at time t (g/g)

k₁ is kinetic constant and k₂ is characteristic constant.

In Eq. 11, ± becomes “+” if there is absorption while “-” is used if desorption occurs.

As per the Exponential association model,

$$S = [1 - \exp(-k_{R2}t)] \quad \dots (12)$$

where, k_{R2} is the kinetic constant (h⁻¹).

When a particular parameter is reported as a function of time and shows either an exponential growth or decay, we can intend to use the Exponential association model. Converting Eq. 12 to a straight line equation i.e., y = mx+c, we can plot a graph between log(S/S₀) and time and then check the curve fitting by estimating the correlation coefficient, R² values.

2.2.3 Characterization

Fourier Transform Infrared Spectroscopy of CS hydrogels

The Infrared Spectral analysis data for CS crosslinked with glutaraldehyde hydrogel was collected by making KBr disc with its powdered sample. Agilent Technologies Spectrophotometer was used for this purpose in the region 4000-650cm⁻¹ at a resolution of 4cm⁻¹.

Thermogravimetric Analysis and Differential Scanning Calorimetry

The decomposition of crosslinked CS hydrogels in powdered form was performed under dynamic nitrogen flow with ramp 10°C/min using TA Instruments, USA, Thermogravimetric Analyser (Q-500). The temperature range was kept between 30°C and 500°C. The thermal properties of hydrogel were assessed using DSC unit Q-200, TA Instruments, USA while the temperature range was kept between 30°C and 500°C with a heating rate of 10°C/ min under nitrogen atmosphere.

3 Results and Discussion

3.1 Selection of hydrogel based on swelling ability

Three different shapes of CS hydrogels were prepared uncrosslinked CS beads, uncrosslinked CS films and CS disc shaped hydrogels crosslinked with low concentrations of glutaraldehyde (as disc shaped hydrogels can be synthesized on addition of crosslinker or using irradiation techniques). CS powder, passed through a particular mesh size was not used for comparison of swelling since CS does not dissolve in water but dissolves in mild acids. The beads having a diameter of 0.3cm displayed a swelling of about 100-200% at pH 7 and even lower swelling in alkaline pH. CS has an effective pK_a of 6-6.5³⁰. Above this value, CS is insoluble whereas below this value, CS is soluble. Since, the uncrosslinked CS materials dissolve in acidic solutions, the values for swelling in acidic conditions is not stated. Swelling results for uncrosslinked CS beads of about 80% have been obtained in another study³¹ at pH 7 whereas this study shows a slightly better swelling of about 100-200%. The square film of size 2.5cm×2.5cm, dissolved in acidic pH and displayed the best swelling at pH 7, which was about 3000%, but the handling was difficult. The flat 2D shaped film, rolled and converted itself into a 3D hollow tubular shape by absorbing water. The absorption was rapid in this

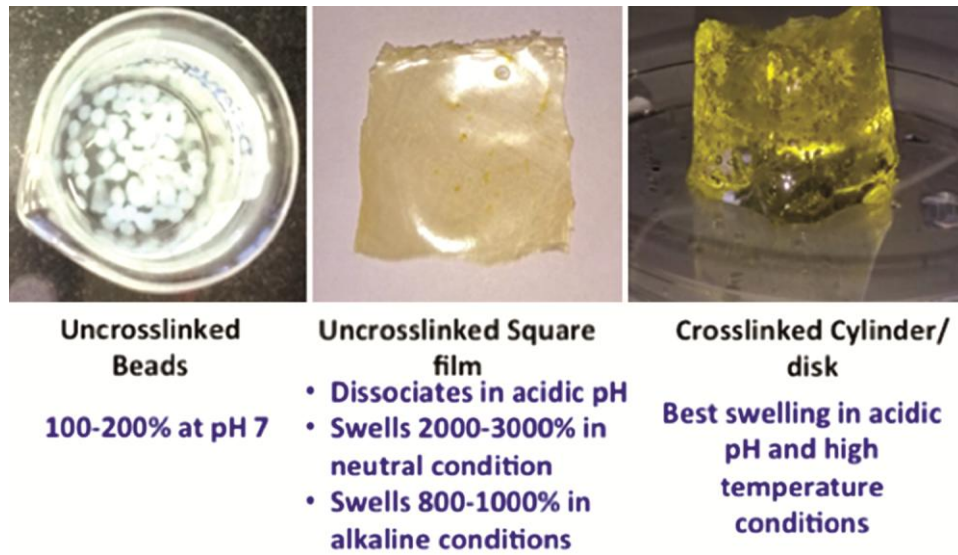


Fig. 2 — Different shapes/ geometries of prepared CS hydrogels.

case. Since CS dissolves in mild acids, this hydrogel dissociated at low pH values.

In another study on CS films, the swelling of uncrosslinked CS films was found to be about 1000%¹¹. The slight differences in swelling in this study may be due to the differences in the molecular weight of CS or the degree of deacetylation. Figure 2 depicts the different shapes of prepared CS hydrogels. In terms of good swelling and ease of handling, crosslinked disc shaped hydrogels having diameter 1cm and thickness 0.4cm were chosen for further assessment.

3.2 Crosslinked CS disc shaped hydrogels - Swelling Results

3.2.1 Effect of pH

The Equilibrium Swelling (ES%) was calculated using Eq. 2. The ES% results have been obtained in triplicate and the mean values have been plotted. Figure 3 depicts the effect of pH on the swelling of hydrogels with varying crosslinker concentrations. CS is a weak polybase/ polyelectrolyte with a pKa around 6.5³². It can be observed that at low pH, i.e. in acidic range, the protonation of amino groups takes place. This leads to repulsion in polymer chains and rupture of intramolecular hydrogen bonding that allows more water to enter into the gel network. The swelling decreases as the pH increases. Least swelling can be seen in case of alkaline pH (10.5) which could be explained by the occurrence of deprotonation of amino groups and repulsion in polymer chains becoming significantly less that leads to shrinking. Therefore, lesser water tends to enter the network. Crosslinking makes the network more compact¹.

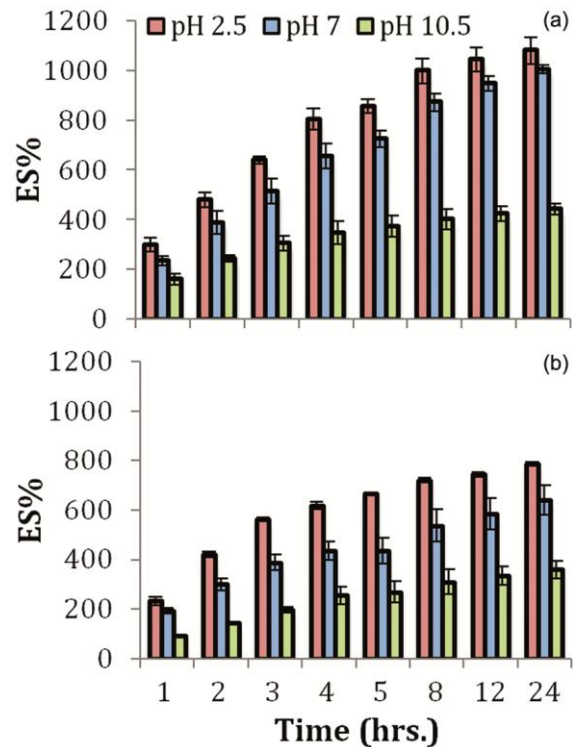


Fig. 3 — Effect of pH on equilibrium swelling (a) CS₁Gl_{0.2}, and (b) CS₁Gl_{0.4}.

Thus, it can be understood that when the crosslinker concentration is increased, the equilibrium swelling gets reduced. When the crosslinker concentration was increased to 0.6mL, it leads to the collapse of the hydrogel matrix. The hydrogel formation with 0.6mL crosslinker occurred in the beaker during mixing and swelling was also significantly low as compared to the other presented compositions.

3.2.2 Effect of temperature

The temperature dependent equilibrium swelling pattern of CS hydrogels with varying crosslinker concentrations is shown in Fig. 4. The swelling was observed in deionized water with pH=7 at a temperature range of 20°-40°C. It can be seen that as the temperature increased, the swelling also increased. A temperature responsive swelling behavior was observed which may be attributed to association (in case of low temperatures) or breakdown (at high temperatures) of hydrogen bonds connecting the amino groups¹¹.

3.2.3 Effect of ionic strength of salts

An increase in the ionic strength from 0.001M to 0.1M NaCl, shows a significant decrease in the equilibrium swelling. This might be due to the fact that osmotic pressure difference decreases between the polymer network and the external solution with increase in ionic strength³³. Moreover, CS is a cationic polyelectrolyte through protonation of amine groups. This generally does not have the tendency to interact with sodium or potassium cation. The absorption of salt solutions would thus be less through these hydrogels. The lesser the molar salt

concentration, the more would be the swelling. This trend is clearly shown in Fig.5.

3.3 FTIR of raw CS and CS hydrogel crosslinked with Glutaraldehyde

FTIR studies were performed with CS₁GI_{0.4} crosslinked hydrogel as this showed a good texture and handling strength. The spectra of raw CS have also been taken into consideration in order to know the changes after crosslinking with glutaraldehyde. The FTIR spectrum for both raw CS and CS₁GI_{0.4} crosslinked hydrogel presented in Fig. 6(a) shows a broad band between 3200-3400cm⁻¹ signifying the presence of hydroxyl group, which is responsible for hydrophilicity of CS³⁴. A sharp peak in the region around 1515-1570cm⁻¹ depicts amide II group³⁵. The observed sharp peak around 1400 cm⁻¹ may be assigned to CH₃ symmetrical deformation mode³⁶. A small peak at 1150cm⁻¹ displays antisymmetric stretching of C-O-C bonds. Bands between 1020-1080cm⁻¹ (C-O stretching involving skeletal vibration) are characteristic of saccharide structure of CS³⁷. A small peak can be observed in case of CS₁GI_{0.4} at 1650cm⁻¹ that shows presence of amide I band which is a characteristic of CS and C=N

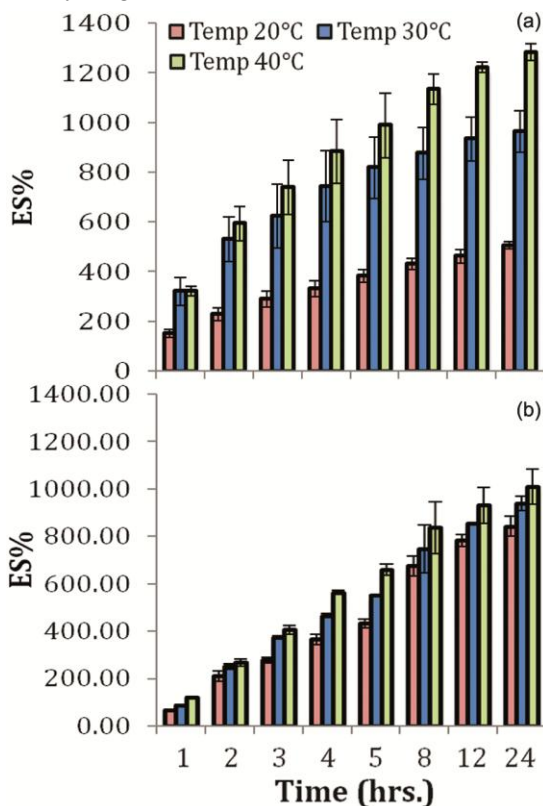


Fig. 4 — Effect of temperature on equilibrium swelling (a) CS₁GI_{0.2}, and (b) CS₁GI_{0.4}.

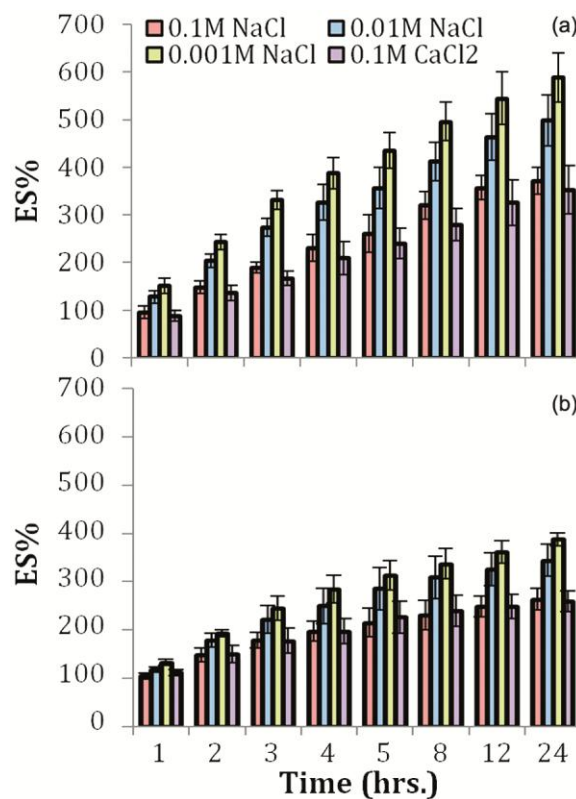


Fig. 5 — Effect of salts on equilibrium swelling (a) CS₁GI_{0.2}, and (b) CS₁GI_{0.4}.

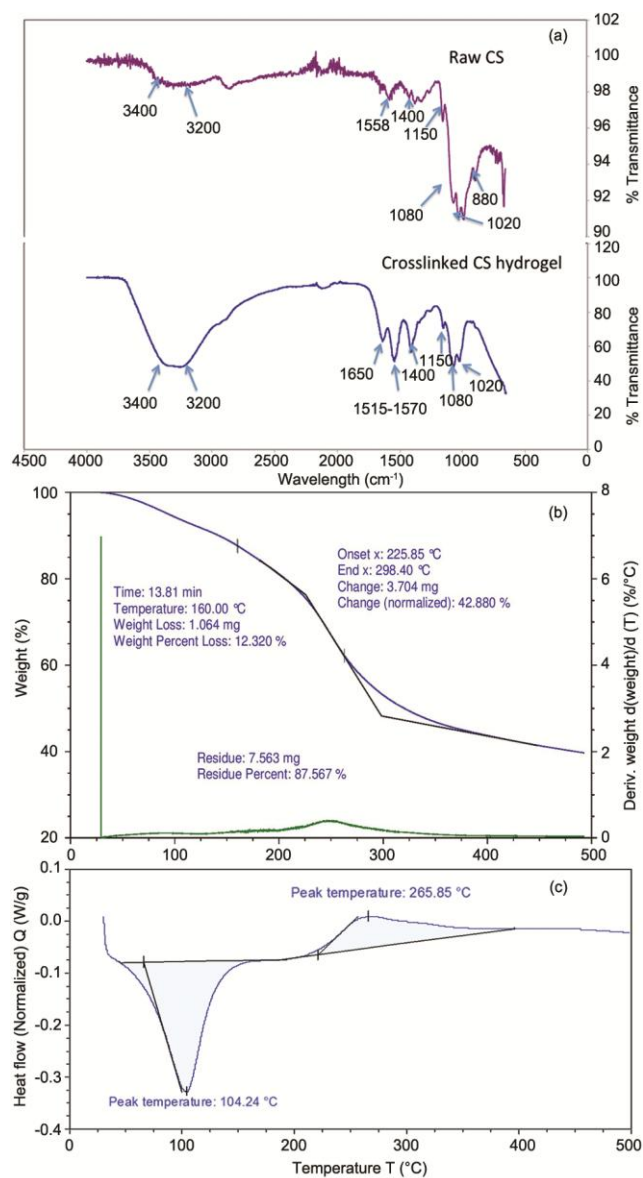


Fig. 6 — (a) FTIR, (b) TGA, and (c) DSC of CS crosslinked with glutaraldehyde.

stretching band of Schiff's base³⁵. This new peak confirms reaction between CS and Glutaraldehyde resulting in formation of imines that are Schiff bases. So, covalent crosslinking can be observed in case of CS and Glutaraldehyde.

3.4 Thermogravimetric analysis and Differential Scanning Calorimetry

CS crosslinked with glutaraldehyde tends to follow a two-stage decomposition process with a minor first stage and major second stage decomposition (Fig. 6(b)). Based on available literature, the decomposition temperature range was varied from

30°C to 500°C. During the first stage, loss of residual, bound or absorbed water present in the polymeric network is achieved by evaporation. By about 160°C, around 12% loss of weight occurs³⁸. The weight loss amount depends on factors such as hydrophilicity, crystallinity and structure of the polymer³⁹. The maximum weight loss (about 43%) can be observed between 225 and 298°C. This attributes to the second stage decomposition, which occurs due to splitting of monomeric units and conversion of complex molecules to simpler ones like acetic acid and lower fatty acids from the used materials. Chemical modification generally leads to a decrease in thermal stability of CS but is essential for improving its applicability in different fields^{39, 40}. As per the study of Ostrowka-Czubenko, the thermal stability decreased when CS was modified with glutaraldehyde and sulfuric acid. But these agents were essential for improving the mechanical strength and acid stability of CS.

In Fig. 6(c), two broad peaks could be observed. The first peak i.e. endothermic peak relates to evaporation of water bound to CS network and the functional groups of glutaraldehyde by hydrogen bonds or other interactions. The second peak that occurs at about 266°C is the exothermic peak, which shows the degradation/melting of main chain of CS³⁹.

3.5 Swelling Kinetics

3.5.1 Order

First Order Kinetics

Plot of ' $\ln(S_{eq}/(S_{eq}-S))$ ' against ' t ' for the crosslinked CS hydrogels represents graph of First order kinetics.

If the swelling is diffusion controlled and obeys Fick's laws, the polymers tend to follow first order kinetics⁴¹. But the R^2 values for First Order Kinetics (presented in Table 2) of these hydrogels need to be compared with the second order R^2 values in order to find out the order of swelling kinetics.

The R^2 values are the deciding factors for predicting the order of kinetics. The closer the values are to 1, the better it follows that order.

Second Order Kinetics

Second order Kinetics plots have been depicted for different Environmental conditions in Fig. 7. During extensive swelling studies, the polymer swelling is not only based on diffusion based on Fick's laws but there is some stress relaxation also by the amorphous

Table 2 — First order R² values for CS hydrogels

Condition	First Order Kinetics	
	CS ₁ Glut _{0.2} R ²	CS ₁ Glut _{0.4} R ²
pH 2.5	0.9894	0.9196
pH 7	0.9971	0.9866
pH 10.5	0.9668	0.9789
Temp 20°C	0.9761	0.9848
Temp 30°C	0.9826	0.9989
Temp 40°C	0.9957	0.9968
0.1M NaCl	0.9946	0.9759
0.01M NaCl	0.9946	0.972
0.001M NaCl	0.9898	0.9646
0.1M CaCl ₂	0.9937	0.9581

Table 3 — Second order kinetics parameters for CS hydrogels

Second Order Kinetics for CS ₁ Gl _{0.2}				
Parameter	S _{eq} (obtained)	S _{eq} (calculated)	K ²	R ²
pH 2.5	1081.17	1428.57	2.04 × 10 ⁻⁴	0.9899
pH 7	1006.74	1428.57	1.44 × 10 ⁻⁴	0.9924
pH 10.5	443.9	500	1.05 × 10 ⁻⁴	0.9976
Temp. 20°C	506.63	588.23	5.78 × 10 ⁻⁴	0.9974
Temp. 30°C	965.67	1111.11	4.05 × 10 ⁻⁴	0.9964
Temp. 40°C	1283.13	1666.66	1.63 × 10 ⁻⁴	0.9938
0.1M NaCl	371.7	500	4.39 × 10 ⁻⁴	0.9969
0.01M NaCl	498.06	625	4.19 × 10 ⁻⁴	0.9978
0.001M NaCl	587.76	714.28	3.92 × 10 ⁻⁴	0.9961
0.1M CaCl ₂	352.49	434.78	5.23 × 10 ⁻⁴	0.9941
Second Order Kinetics for CS ₁ Gl _{0.4}				
Parameter	S _{eq} (obtained)	S _{eq} (calculated)	K ²	R ²
pH 2.5	787.22	909.09	5.04 × 10 ⁻⁴	0.9875
pH 7	642	714.28	5.29 × 10 ⁻⁴	0.9994
pH 10.5	360.38	434.78	6.61 × 10 ⁻⁴	0.99
Temp. 20°C	842.63	2000	2.84 × 10 ⁻⁵	0.9173
Temp. 30°C	939.9	1666.66	5.80 × 10 ⁻⁵	0.9739
Temp. 40°C	1010.21	1666.66	6.66 × 10 ⁻⁵	0.9073
0.1M NaCl	263.98	285.71	2 × 10 ⁻³	0.9994
0.01M NaCl	343.98	384.61	1.18 × 10 ⁻³	0.9975
0.001M NaCl	387.79	434.78	1.03 × 10 ⁻³	0.9977
0.1M CaCl ₂	259.52	285.71	2.11 × 10 ⁻³	0.9973

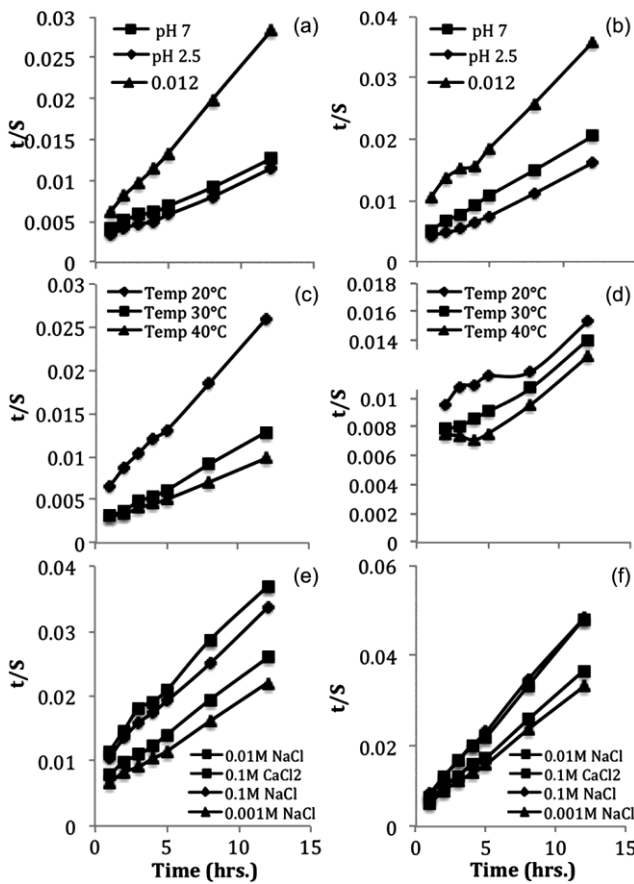


Fig. 7 — Second order kinetics plots (a) CS₁Gl_{0.2} at different pH, (b) CS₁Gl_{0.4} at different pH, (c) CS₁Gl_{0.2} at different temperatures, (d) CS₁Gl_{0.4} at different temperatures, (e) CS₁Gl_{0.2} at different molar salt concentrations, and (f) CS₁Gl_{0.4} at different molar salt concentrations.

portion or macromolecular chains of the polymeric network²⁵. So, based on R² values, the polymers tend to follow, second order kinetics as can be depicted from Table 3.

3.5.2 Diffusion of Water

The Diffusion exponent values for different parameters are given in Table 4.

Alfrey *et al.*⁴¹ described three cases of solvent diffusion into the polymeric network.

Case I- is Fickian diffusion (n=0.5) in which the polymer chains relaxation rate is faster than the diffusion of solvent inside the network.

Case II- is non-Fickian diffusion (n=1) in which the diffusion of solvent is faster than polymer chains relaxation rate.

Case III- is Anomalous diffusion (0.5<n<1) in which the rate of diffusion and polymer chain relaxation is almost the same.

Most of the swelling exponent parameter values for different conditions indicate Case III or Anomalous diffusion mechanism since 0.5<n<1. In such cases, the polymer chains do not permit immediate penetration of solvent and it takes time for water to enter till the core³⁹.

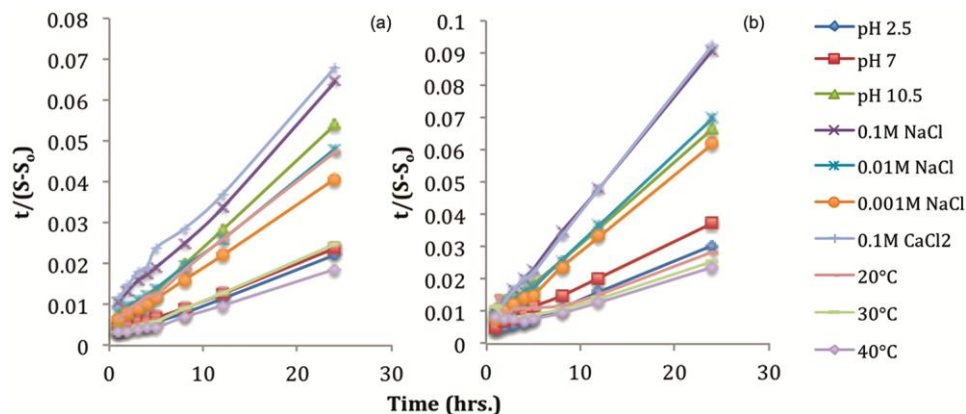
3.5.3 Absorption kinetics modeling

Peleg's model

In order to get an idea of the model that is being followed during absorption, graphs were interpolated

Table 4 — Swelling Kinetics parameter values

CS ₁ GI _{0.2}						
Parameter	Swelling after 24 h (g/g)	EWC	Diffusion Exponent (n)	R ²	Diffusion Constant [k (s ⁻¹)]	Diffusion Coefficient [D (m ² s ⁻¹)]
pH 2.5	10.81	91.5	0.69	0.9999	10.05	2.17 × 10 ⁻³
pH 7	10.06	90.96	0.71	0.9991	10.174	1.02 × 10 ⁻³
pH 10.5	4.43	81.55	0.59	0.9997	9.9213	9.37 × 10 ⁻⁴
Temp. 20°C	5.06	83.5	0.58	0.9989	10.297	1.60 × 10 ⁻³
Temp. 30°C	9.65	90.51	0.73	0.9805	9.918	2.24 × 10 ⁻³
Temp. 40°C	12.83	92.76	0.76	0.9869	9.9371	1.75 × 10 ⁻³
0.1M NaCl	3.71	78.65	0.62	0.9998	10.345	1.39 × 10 ⁻³
0.01M NaCl	4.98	82.98	0.69	0.9993	10.184	1.38 × 10 ⁻³
0.001M NaCl	5.87	85.29	0.71	0.9981	10.155	1.72 × 10 ⁻³
0.1M CaCl ₂	3.52	77.28	0.54	0.9961	10.445	9.22 × 10 ⁻⁴
CS ₁ GI _{0.4}						
Parameter	Swelling after 24 h (g/g)	EWC	Diffusion Exponent (n)	R ²	Diffusion Constant [k (s ⁻¹)]	Diffusion Coefficient [D (m ² s ⁻¹)]
pH 2.5	7.87	88.73	0.85	0.9982	9.6821	1.62 × 10 ⁻³
pH 7	6.42	86.36	0.63	0.9999	10.092	1.19 × 10 ⁻³
pH 10.5	3.6	77.99	0.68	0.9982	10.183	7.94 × 10 ⁻⁴
Temp. 20°C	8.42	89.35	0.84	0.9642	10.248	9.63 × 10 ⁻⁴
Temp. 30°C	9.39	90.37	0.86	0.975	10.15	1.91 × 10 ⁻³
Temp. 40°C	10.1	90.92	0.9	0.9995	10.102	1.37 × 10 ⁻³
0.1M NaCl	2.63	72.31	0.5	0.9995	10.073	1.91 × 10 ⁻³
0.01M NaCl	3.43	77.21	0.6	0.9989	10.039	1.65 × 10 ⁻³
0.001M NaCl	3.87	79.47	0.55	0.9994	10.125	2.51 × 10 ⁻³
0.1M CaCl ₂	2.59	71.96	0.42	0.9999	10.186	2.62 × 10 ⁻³

Fig. 8 — Plot of $t/(S-S_0)$ and t for (a) CS₁GI_{0.2} hydrogels, and (b) CS₁GI_{0.4} hydrogels at different conditions.

using Peleg's and exponential association equations. Figure 8 shows the plots obtained for hydrogel as per Peleg's model. The parameter values for initial and maximum absorption have been calculated and presented in Table 5.

The R^2 values were around 0.99 in most cases, which displayed that the swelling degree fitted well with this model. Similar swelling values fitting well with Peleg's model have been obtained for Gelatin-Carboxymethyl CS hydrogels. It may be noted that the lower the value of k_1 , more would be the initial absorption rate. Lower the k_2 , higher is the maximum

water absorption capacity⁴². The values of k_1 and k_2 are lower in case of acidic pH, high temperature and lower molar salt concentrations.

Exponential Association model

The graphs for this model have been presented in Fig. 9. The R^2 values obtained through Exponential Association model lied in the range 0.54-0.78 and were thus comparatively much lower than the R^2 values obtained in Peleg's model. Thus, the water diffusion in hydrogels follows the Peleg's model and does not show an exponential behavior.

Table 5 — Parameter values for Peleg’s model at different swelling conditions

Peleg's Model parameter values at various swelling conditions

CS ₁ GI _{0.2} Swelling Condition	k ₁	k ₂	R ²	RMSE	χ ²
pH 2.5	0.002	0.0008	0.9945	0.00049	0.0003
pH 7.0	0.0029	0.0009	0.9945	0.00065	0.0004
pH 10.5	0.0035	0.0021	0.9991	0.00045	0.00015
20°C	0.0047	0.0018	0.9982	0.000606	0.0002
30°C	0.0017	0.001	0.9978	0.00057	0.00028
40°C	0.0018	0.0007	0.9932	0.00041	0.00032
0.1M NaCl	0.0079	0.0023	0.9956	0.00109	0.00036
0.01M NaCl	0.0056	0.0018	0.9985	0.00066	0.00019
0.001M NaCl	0.0046	0.0015	0.9981	0.00045	0.00016
0.1M CaCl ₂	0.0099	0.0024	0.9959	0.00108	0.00039
CS ₁ GI _{0.4}					
pH 2.5	0.0021	0.0012	0.9966	0.00056	0.00047
pH 7.0	0.0066	0.0002	0.7329	0.00027	0.000056
pH 10.5	0.0073	0.0024	0.9966	0.00106	0.00049
20°C	0.0088	0.0007	0.8102	0.0028	0.0072
30°C	0.0065	0.0007	0.8935	0.0019	0.0049
40°C	0.0052	0.0007	0.9434	0.00128	0.0015
0.1M NaCl	0.005	0.0036	0.997	0.00049	0.000039
0.01M NaCl	0.0052	0.0027	0.9989	0.00068	0.0002
0.001M NaCl	0.0048	0.0024	0.9985	0.00072	0.00026
0.1M CaCl ₂	0.0053	0.0036	0.9991	0.00074	0.00019

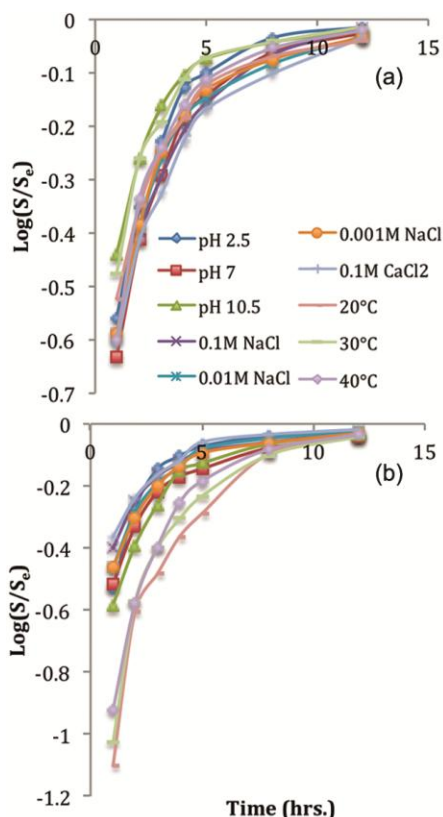


Fig. 9 — Plot of Log (S/S_e) and time for (a) CS₁GI_{0.2} hydrogels, and (b) CS₁GI_{0.4} hydrogels at different conditions.

4 Conclusion

At the outset, different shapes of CS hydrogels were synthesized using either physical mechanisms such as drying or using chemical crosslinking agents such as glutaraldehyde. Glutaraldehyde was chosen as the crosslinker as the reaction with it is very fast and we require a relatively low concentration of the chemical for the reaction. It is also economical, easy for procurement and gives stable products that can tolerate wide pH shifts. Physically formed hydrogels were in the form of beads and square film while the crosslinked hydrogels were cut in cylindrical discs. The least swelling (100-200%) was observed in case of beads whereas it was most in film shape hydrogel (2000-3000%). Since the crosslinked disc shaped hydrogels were rigid and much easier to handle, further swelling kinetics studies were conducted using them.

FTIR spectrum of disc hydrogels revealed presence of hydrophilic groups like hydroxyl and amide, which are responsible for water absorbing properties of CS. Best swelling equilibrium values of 10.81, 12.83 and 5.87 g of solvent/g of hydrogel respectively were attained at acidic pH, temperature of about 40°C and low ionic concentration of 0.001M NaCl in case of CS₁Glut_{0.2} (hydrogel prepared with lower concentration of crosslinker). Enhancement in the crosslinker concentration led to formation of hydrogels with a better mechanical strength but the equilibrium swelling capacity decreased.

Based on the statistical assessment, the synthesized CS hydrogels followed the second order kinetics. The diffusion was found to be Non-Fickian and Anomalous in most of the cases and it seemed that immediate solvent penetration could not be possible as temperature of polymer was lower than its glass transition temperature. To determine the water absorbed by hydrogels under different environmental conditions, Peleg’s model and Exponential association model were used. Out of the two, Peleg’s model proved to show a good agreement with the experimental data.

The scientific insights of this study on CS hydrogels are:

- CS has been identified as a biocompatible material whose shapes and properties could be tuned by changing the environmental conditions or stimulus. For example, physically synthesized CS hydrogels could be used for drug delivery in

stomach where pH is low. The hydrogel could undergo dissociation and release the drug.

- The best shape in terms of maximum swelling is a thin film which on absorption of water turns to a 3D hollow tube. The mechanical strength of this tube can be enhanced by grafting it with other synthetic polymers such as acrylic acid, acrylamide or natural polymers such as cellulose. This change of shape property could be of use in soft robotics.

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