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Synthesis And Characterisation of Composite Hydrogels Based on Chitosan, Gelatin and Carbon Black

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Abstract: Hydrogels based on gelatin and chitosan were created by cross-linking with glutaraldehyde. Carbon Black (CB) is utilised as an ingredient in the production of composite hydrogels. DSC, TGA, FTIR, and XRD were used to characterise the gels that were created. The gels were discovered to have excellent mechanical and thermal characteristics. Swelling experiments were carried out in acidic, neutral, and basic environments and found outstanding results. When the concentration of CB increases tenfold in acidic conditions, at pH 1.2 and 4.0, the percentage swelling increases. However, when the concentration of CB increases, the percentage swelling decreases. Swelling diminishes gradually with increasing CB concentration in neutral and basic mediums at pH 7.0 and 9.0 respectively. Similarly, no trend was found when the content of glutaraldehyde was varied in the acidic medium. However, in neutral and acidic conditions, the percentage of swelling reduces as the content of glutaraldehyde increases from 2 to 8%. In all pH circumstances, the proportion of swelling reduces steadily as the amount of chitosan increases from 0.5 to 1.5%. The gel content was calculated for all gels and ranged from 71 to 85%.

Keywords: Hydrogels, cross-linking, swelling, deacetylation, gel content

1.Introduction

A hydrogel is a cross-linked polymer network that can absorb significant amounts of water while maintaining its network structure in a swelled condition [1]. Hydration of hydrophilic groups or domains in an aqueous environment produces the hydrogel structure [2]. Hydrogels can be made by combining different polymers or monomers in the presence of appropriate cross-linkers and initiators and then drying them. Hydrogels made from natural polymers such as chitosan are fragile, but their mechanical qualities can be enhanced by blending with additional polymers or cross-linking using appropriate cross-linkers [3]. By using suitable nano or other materials, the gel's qualities such as stability, mechanical strength, and swelling behaviour can be enhanced. The current study aims to develop and investigate IPN hydrogels made from chitosan, gelatin and carbon black (CB) that have been cross-linked with glutaraldehyde (GA)

Chitosan is a linear polymer composed primarily of 2-amino-2-deoxy-β-D-glucopyranose units with trace amounts of 2-acetamido-2-deoxy-β-D-glucopyranose units linked by a 1,4-b-glycoside linkage. Chitosan is made via deacetylation of chitin, a polymer found in crustaceans and insects [4]. Gelatin is a water-soluble protein and peptide combination. It is made by controlled hydrolysis of collagen derived from materials such as hides, bones, and pig skin [5].

A straight chain dialdehyde is glutaraldehyde or pentanedial. It works well as a cross-linking agent for collagen-based biomaterials such as gelatin. Cross-linking occurs by the reaction of free amino groups of amino acids such

as lysine in gelatin and the aldehyde group of GA. The initial step involves the creation of Schiff's bases between amino groups and aldehyde groups, which is followed by a series of complex reactions that result in cross-linking [6]. Cross-linking stabilises the hydrogel, although the swelling ratio generally falls, most likely due to a reduction in the amount of space available inside the gel to accommodate water molecules.

2.Materials and Methods

2.1 Materials

Chitosan, gelatin and glutaraldehyde were purchased from Loba Chemie Pvt. Ltd, Mumbai, India. Carbon Black, having surface area 75 m^2 /g and bulk density 170-23 g/L was purchased from Alfa Aesar, USA.

2.2 Methods

2.2.1 Synthesis of hydrogels

The hydrogels were made by combining chitosan and gelatin solutions as mentioned in Table 1 and then adding glutaraldehyde solution. Each gel sample was made from 10 mL of chitosan, gelatin, and glutaraldehyde solutions. A one percent chitosan solution was made by combining 0.1 g chitosan with 10 mL of water containing 1 mL of glacial acetic acid and stirring for 24 hours with a magnetic stirrer. A 6% gelatin solution was made by soaking 0.6 g gelatin in 10 mL water overnight and agitating for one hour. Glutaraldehyde (GA) was provided as a 25% solution that was quantitatively diluted to obtain solutions of specified concentrations. To make the gel, 10 mL chitosan solution and 10 mL gelatin solution were mixed together for two hours before adding 10 mL glutaraldehyde solution. After a few minutes of stirring, the solution was placed into a petri dish and dried in a vacuum oven at 50 ºC to 55ºC and 550 to 600 mm of Hg pressure.

Table 1. Composition of Hydrogels

Sl. No.	Code	Chitosan (%)	Gelatin (%)	GA (%)	CB(g)
1	CG0	1	0	2	0
2	CG1	1	6	2	0
3	CG2	1	6	4	0
4	CG3	1	6	6	0
5	CG4	1	6	8	0
6	CG5	1	4	2	0
7	CG6	1	8	2	0
8	CG7	0.5	6	2	0
9	CG8	1.5	6	2	0
10	CGCB1	1	6	2	0.002
11	CGCB2	1	6	2	0.02
12	CGCB3	1	6	2	0.2

Hydrogels of various compositions were created and coded as shown in Table 1. Carbon Black -containing samples were made using the same method, but a weighed amount of CB was added during the blending of gelatin and chitosan solutions and before adding glutaraldehyde. All the dry gels were obtained in the form of films that were cut into appropriate sizes and then dried individually to constant weight.

2.2.2 Characterisation

Because they comprised the highest amounts of chitosan, gelatin, and CB, the hydrogels CG0, CG6, and CGCB3 were chosen as typical samples for characterisation tests.

2.2.2.1 Scanning Electron Microscopy (SEM)

A JSM 6390 Scanning Electron Microscope (SEM) was used to examine the surface morphology of the selected gels CG0, CG6, and CGCB3. Each gel was photographed at five different magnification levels.

2.2.2.2 Fourier-Transform Infra-Red Spectroscopy (FT-IR)

Thermo Nicolet iS50 FTIR spectrometer was used to obtain FTIR spectra of dry gels in the range 4000 cm^{-1} to 100 cm^{-1} with a resolution of 0.2 cm^{-1}.

2.2.2.3 Differential Scanning Calorimetry (DSC)

DSC analysis was performed on representative gels using the Netzsch DSC 204 F1 at temperatures ranging from 20°C to 400°C. For all three gels, aluminium crucibles with punctured lids were employed.

2.2.2.4 Thermo Gravimetry (TG) and Derivative Thermo Gravimetry (DTG)

The TG and DTG experiments were performed using a Hitachi STA 7300 in the temperature range of RT to 700°C.

2.2.2.5 X-Ray Diffraction (XRD)

The selected gels' XRD data were observed at RT using a Bruker D8 Advance instrument in the angle range of 0 to 80 degrees.

2.2.3 Swelling Studies

A little dry portion of each gel was precisely weighed before being immersed in a pH 7.0 buffer solution. The gel was removed at regular intervals, carefully weighed, and soaked in buffer solution once more. The swelling of each gel was examined for up to 24 hours.

The percentage swelling was calculated as per the equation,

$$S\% = \frac{w_t - w_0}{w_0} \times 100$$

where w_0 and w_t are the masses of dry gel and swollen gel at time 0 & t respectively [7].

The percentage swelling was plotted against time, and the effects of glutaraldehyde, gelatin, chitosan, and CB variations were investigated. The effect of pH change was investigated by comparing the swelling of CG1 in buffer solutions with pH values of 1.2, 4.0, 7.0, and 9.0.

In order to study the swelling kinetics, the ratio $\frac{t}{S}$ was plotted against t, where t is time and S is swelling which is obtained by the equation $S = \frac{w_t - w_0}{w_0}$ where w_0 and w_t are the masses of dry gel and swollen gel respectively. The rate of swelling was calculated as $r = \frac{1}{A}$ where A is the y-intercept of the plot. The equilibrium swelling was calculated as $S_e = \frac{1}{B}$ where B is the slope. Then rate constant for swelling was calculated as $k_s = \frac{r}{S_e^2}$. In this case also the effects of variation of the amounts of GA, gelatin, chitosan, CB and pH were studied as before [8].

For each gel, lnt values were plotted against lnS and swelling constant(K) and swelling exponent (n) were evaluated from the intercept and slope of each plot respectively [9].

2.2.4 Study of Gel Content

A little piece of gel was heated to a consistent weight before being immersed in water for two days. After 48 hours, the bloated gel is removed and heated to constant weight once more. If and are the masses of dry gel before and after 48 hours of soaking and subsequent drying, the gel content is computed as

$$g = \frac{m}{m_0} \times 100$$

3. Results and Discussions

3.1 Scanning Electron Microscopy (SEM)

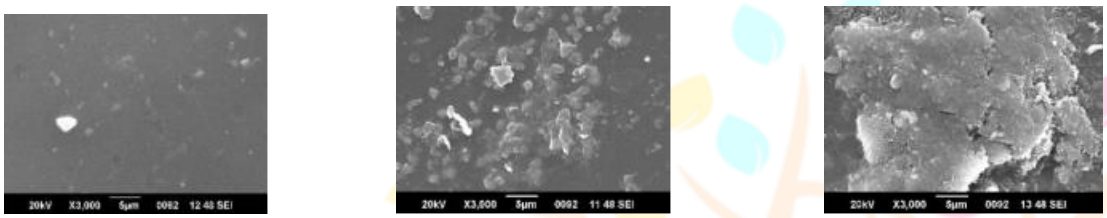
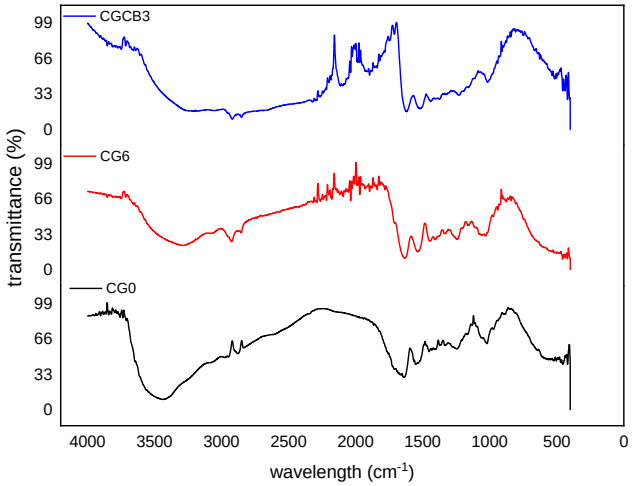


Figure 1. SEM images of (a) CG0 (b) CG6 and (c) CGCB3

Figure 1 depicts SEM images of CG0, CG6, and CGCB3. It is clear from the photographs that CG0 is homogeneous. The addition of gelatin renders the gel heterogeneous, improving the durability of the porous structure and pore wall thickness. The addition of CB enhances mechanical characteristics while decreasing the porosity.

3.2 Fourier-Transform Infra-Red Spectroscopy (FT-IR)

Figure 2 depicts the FTIR spectra of the selected gels CG0, CG6, and CGCB3. Some notable chitosan absorptions in the IR region occur at 1320 cm^{-1} and 3350 cm^{-1} due to N-acetyl glucosamine, as well as at 1420 cm^{-1} due to glucosamine [10]. All these components are present in all three gels, demonstrating the presence of chitosan in the produced gels. Gelatin absorbs at 1328 cm^{-1} (due to the proline side chain), 1541 cm^{-1} (related to peptide N-H deformation), and 3270-3370 cm^{-1} (due to peptide N-H stretching) [11]. All of them are present in the CG6 and CGCB3 spectra, demonstrating the existence of gelatin in the dry gel. The interaction of CB with other components causes the broad absorption from 2300 cm^{-1} to 3200 cm^{-1} in CGCB3.



3.3 Differential Scanning Calorimetry (DSC)

Figure 3 depicts the DSC analysis data for the selected gels CG0, CG6, and CGCB3. The early endothermic changes in all gels up to 200oC are caused by the loss of water absorbed in the gel by diverse processes such as physisorption, chemisorption, hydrogen bonding, and electrostatic attraction. Exothermic reactions occur above 200ºC due to monomer breakdown [12, 13]. Monomer breakdown occurs at higher temperatures as well. The glass-transition temperatures of the selected gels were 162ºC, 213ºC, and 197.4ºC, respectively for CG0, CG6, and CGCB3. Tg value increased with the addition of gelatin and dropped with the addition of CB.

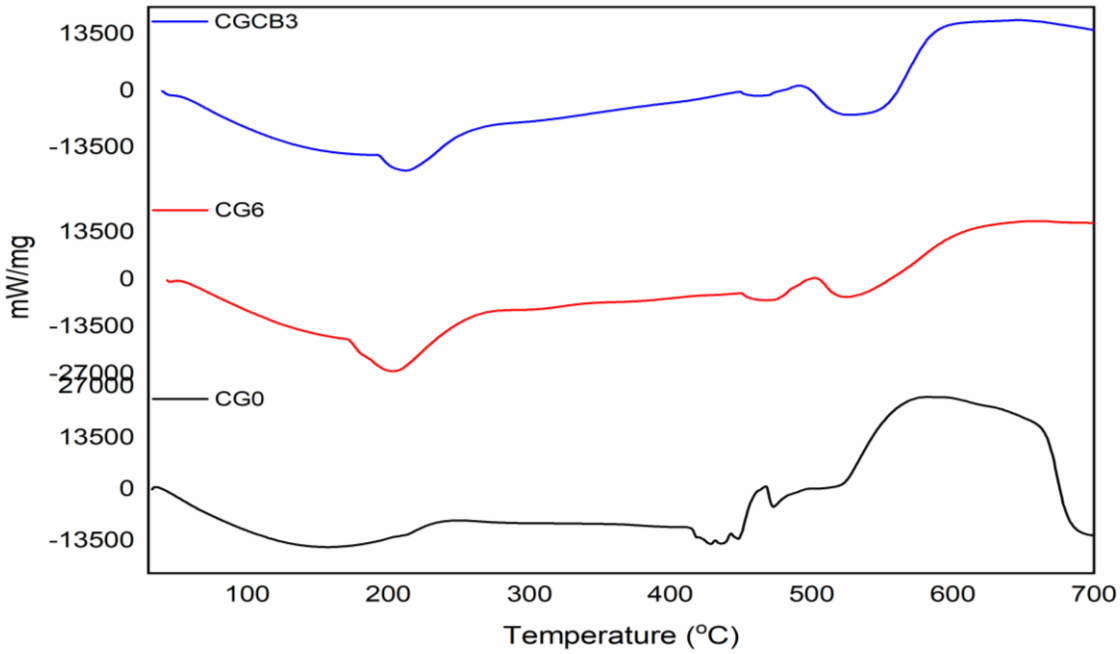


Figure 3. DSC data

2.2.2.4 Thermo Gravimetry (TG) and Derivative Thermo Gravimetry (DTG)

Figure 4 depicts the TG curves of CG0, CG6, and CGCCB3 produced by graphing the percentage change in mass of the sample with temperature. The thermal stabilities of the gels clearly rise from CG0 to CGCB3. DTG curves were generated by graphing the rate of change of mass with time versus temperature. Figure 5 shows the DTG curves for CG0, CG6, and CGCB3. There are multiple thermal events visible in the DTG curve of CG0, which is cross-linked chitosan. One begins before 60ºC and finishes about 150ºC. This is due to the loss of water in the

gel [14]. The second event, which occurs at 200°C, is caused by polymer breakdown into monomers. Monomer degradation occurs between 400°C and 500°C.

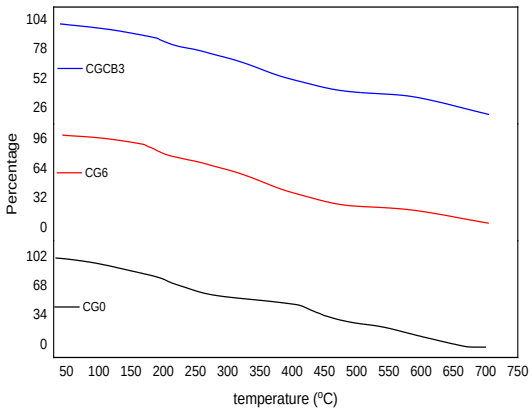


Figure 4. TG curves

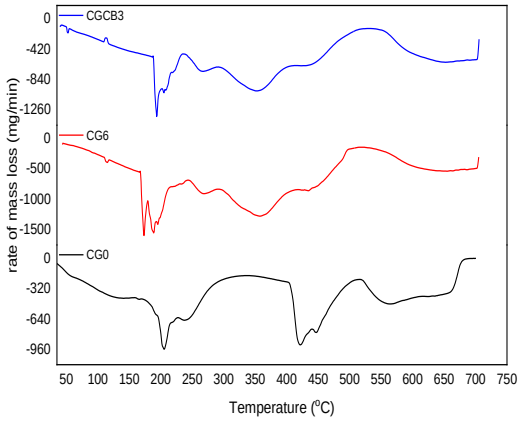


Figure 5. DTG curves

Dehydration peaks at 114°C and polymer degradation peaks at 173.5°C and 188.8°C are visible on the CG6 curve, respectively. At 269°C and 355°C, monomers begin to degrade. Pure gelatin dehydrates and degrades at 126°C and 326°C, respectively [11]. These values are somewhat altered since CG6 contains chitosan mixed with gelatin and cross-linked with GA. CGCB3's DTG curve is similar, but with a little temperature shift due to the presence of CB. The dehydration and degradation peaks of hydrogels will vary depending on the presence of other substances since interactions between different components may alter the level of hydration, thermal stability, and so on.

2.2.2.5 X-Ray Diffraction (XRD)

The XRD data of the gels are shown in Figure 6. In the case of CG0, which contains only cross-linked chitosan, there is a broad peak at $2\theta = 20°$. This corresponds to a characteristic peak for pure chitosan [15]. In CG6, there is a broad peak around $2\theta = 14°$ which is characteristic for gelatin [11]. In CGCB3, there are two peaks around $2\theta = 26°$ and $2\theta = 43°$ which are characteristic peaks for CB [16].

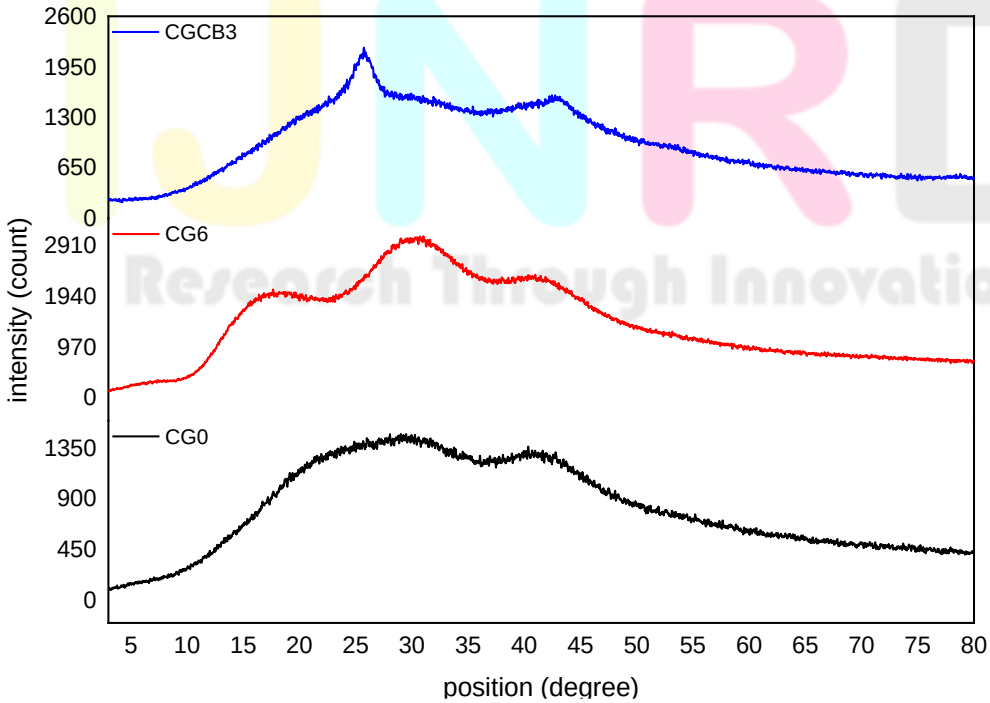


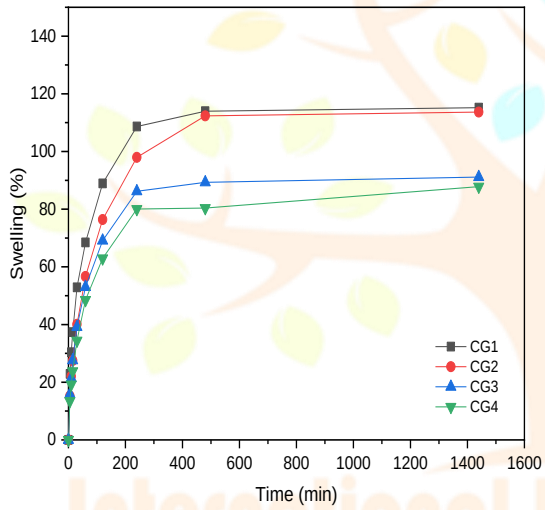
Figure 6. XRD data

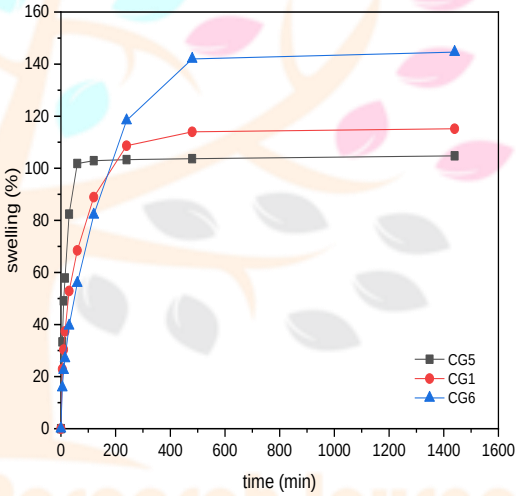
3.5 Swelling Studies

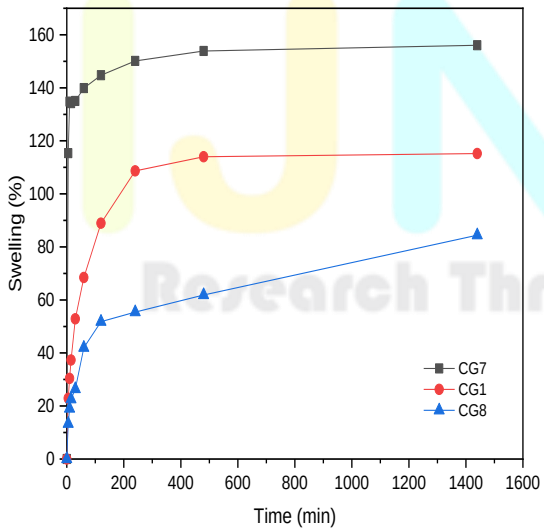
3.5.1 Percentage Swelling

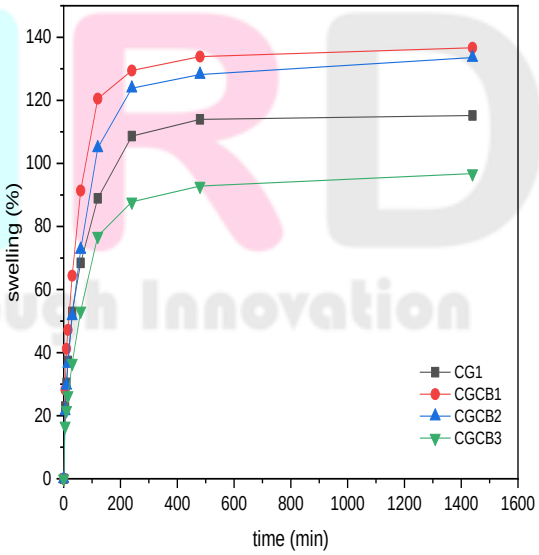
Figures 7a to 7e show the swelling vs. time plots. By contrasting the swelling behaviours of CG1, CG2, CG3, and CG4, the impact of varying the amount of GA on the percentage swelling was investigated. Figure 7a illustrates this. As can be observed, the swelling goes down as GA intake increases. The CG1 gel, which has the least amount of GA, exhibits the best swelling behaviour. By contrasting the swelling of CG5, CG1, and CG6, the impact of variations in the amount of gelatin was investigated. Figure 7b illustrates this. CG6 has the best swelling behaviour in this situation. Although CG5 has a high initial swelling, it is less stable and decomposes before reaching its full swelling potential. By contrasting CG7, CG1 and CG8, the impact of chitosan dosage change was investigated. Figure 7c depicts the results of this study. The optimum swelling behaviour of these gels is exhibited by CG7.

By contrasting the swelling of CGCB1, CGCB2, and CGCB3, the effect of varying the amount of added CB on the swelling behaviour of the gel was explored. In Figure 7d, this investigation is depicted. Swelling rises with CB concentration, reaches a maximum at CGCB2, and then falls. By contrasting the swelling of CG1 in buffer solutions of pH 1.2, 4.0, 7.0, and 9.0, the impact of pH change on swelling was investigated. In Figure 7e, this variation is displayed. No consistent pattern exists in the relationship between pH and swelling. At pH 1.2, the gel behaves best in terms of swelling, while at pH 4.0, it behaves worst.









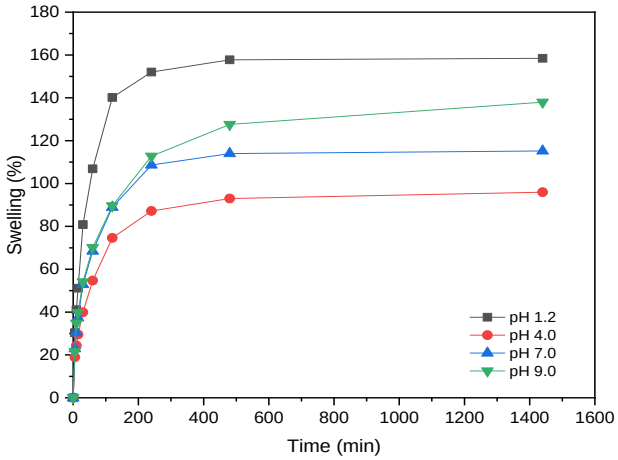


Figure 7. Swelling percentage curves as a function of (a) GA (b) gelatin (c) Chitosan (d) CB & (e) pH

3.5.2 Kinetics of Swelling

The ratio $\frac{t}{S}$ was plotted against t for the matching gels to evaluate the influence of variation in GA, gelatin, chitosan, CB, and pH on swelling kinetics. Figures 8a and 8b show the plot. The initial rate of swelling, r equilibrium swelling, 'S_e' and swelling rate constant, ks were determined and are shown in Table 2. According to the table, 'S_e' values estimated theoretically from slope are in good agreement with swelling % calculated experimentally. The initial swelling rate reduces as the amount of GA, gelatin, and chitosan increases. This is conceivable because increasing these parameters tightens the structure, making it more difficult for water to diffuse into the gels.

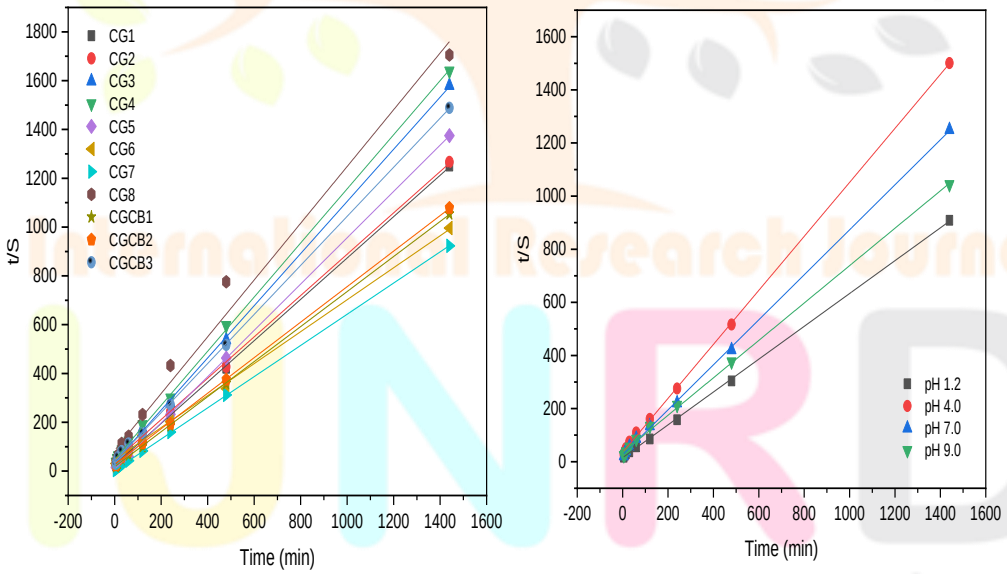


Figure 8. Swelling rate curves as a function of (a) GA, gelatin, Chitosan, CB & (b) pH

3.5.3. Mechanism of Swelling

The slopes and intercepts of the lines of lnS versus lnt were used to compute the swelling exponent, 'n,' and swelling constant, 'K,' with variations in GA, gelatin, chitosan, CB, and pH. Figures 9a and 9b show the plots, while Table 2 shows the values. The 'n' values of the gels increased significantly as the amount of gelatin increased. The "n" value increases from 0.19 to 0.43 when the amount of gelatin is raised from 4% to 8%. In the case of chitosan, the opposite trend was found. The n value reduces from 0.45 to 0.32 as the amount of chitosan increases from 0.5 to 1.5%. The swelling exponent, 'n' value, which is less than 0.5, confirmed that the process of

water transport into the gels might be anomalous diffusion. The variations in the chemical properties of the network structure caused by changes in the GA content, polymer composition, CB content, and pH of the medium were clearly represented in the gels' 'K' values.

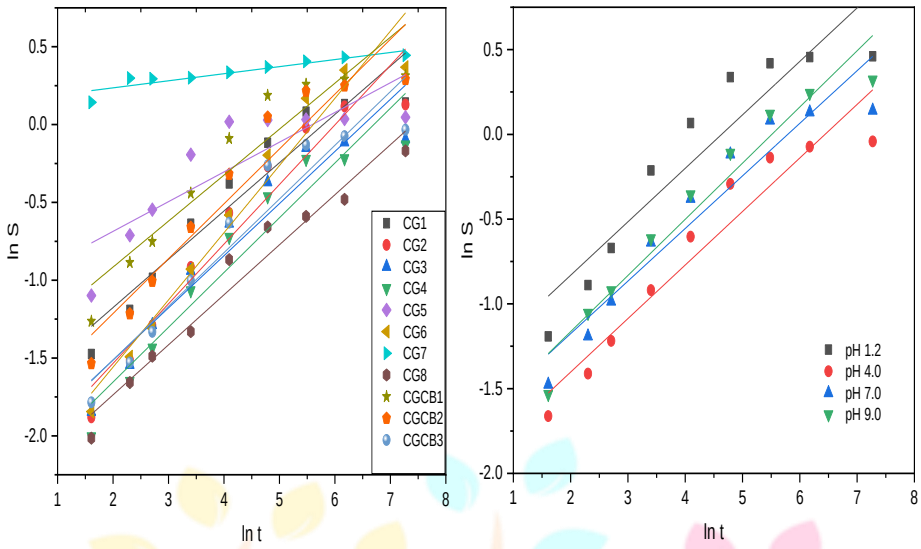


Figure 9. Swelling kinetic curves as a function of (a) GA, gelatin, Chitosan CB & (b) pH

3.6 Gel Content

Table 2 shows the gel composition of the gels that were determined. It was discovered that as the GA concentration increased, the gel content decreased from 78.74 to 59.18. Gel content increases as the amount of gelatin and CB increases. When the gelatin content is increased from 4 to 8%, the gel content rises from 75.31 to 82.04. Similarly, increasing the CB concentration from 0.002 to 0.2%, raises the gel content from 80.04 to 84.46. This shows that the gels with a higher concentration of CB are more stable.

Table 2. Swelling Parameters and Gel Content of Hydrogels

Gel Code	Swelling Percentage, S%	Swelling Rate, r	Equilibrium Swelling, Se %	Rate Constant, ks	Swelling Exponent, n	Swelling Constant, K	Gel content
CG1	115	0.03783	118	0.02781	0.3103	0.16593	78.74
CG2	114	0.02392	118	0.01717	0.3831	0.10020	63.40
CG3	91	0.02752	94	0.03144	0.3350	0.11276	59.18
CG4	88	0.02101	90	0.02585	0.3518	0.09461	62.94
CG5	105	0.13665	105	0.12303	0.1910	0.34360	75.31
CG6	145	0.02113	154	0.00890	0.4317	0.08877	82.04
CG7	156	0.28792	156	0.11764	0.4543	1.15612	82.70
CG8	84	0.01173	85	0.01586	0.3214	0.09262	84.35
CGCB1	137	0.05620	139	0.02897	0.2954	0.22169	80.04
CGCB2	134	0.04983	137	0.02639	0.3524	0.14680	81.90
CGCB3	97	0.02576	99	0.02603	0.3449	0.11050	84.46

4. Conclusions

Hydrogels based on gelatin/chitosan/CB were created with glutaraldehyde as a crosslinker. Carbon Black (CB) is utilised as an ingredient in the production of composite hydrogels. SEM, DSC, TG, and FTIR methods

were used to confirm the composite's production. Swelling experiments were carried out in acidic, neutral, and basic environments, with outstanding results. When the concentration of CB increases tenfold in acidic conditions, at pH 1.2 and 4.0, the percentage swelling increases tenfold. However, when the concentration of CB increases, the swelling reduces. Swelling diminishes gradually with increasing CB concentration in neutral and basic mediums at pH 7.0 and 9.0, respectively. Similarly, no trend was found when the content of glutaraldehyde was varied in the acidic medium. However, in neutral and acidic conditions, the percentage swelling reduces as the content of glutaraldehyde increases from 2 to 8%. In all pH circumstances, the percentage swelling reduces steadily as the amount of chitosan increases from 0.5 to 1.5%. It was discovered that theoretically derived 'S_e' values from the slope agree well with experimentally obtained swelling percentages. The initial swelling rate reduces as the amount of GA, gelatin, and chitosan increases. The swelling exponent, "n" value increases from 0.19 to 0.43 when the amount of gelatin is raised from 4% to 8%. However, as the amount of chitosan increases from 0.5 to 1.5%, the n value falls from 0.45 to 0.32. The swelling exponent, 'n' value, which is less than 0.5, confirmed that the process of water transport into the gels might be anomalous diffusion. The gel composition of all the gels was also calculated, and it ranged from 71 to 85%. All gels contain a significant gel content and are stable. In this gel system, more research might be done by substituting various nanoparticles for CB. These gels' use in medicine delivery, agriculture, and other fields may be investigated.

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