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Article

Preparation and Evaluation of the polyelectrolyte complex of Chitosan/Carrageenan Cross-Linked with Glutaraldehyde

Zahraa T. Hano, Tahseen A. Saki[a], Bushra A.A. Al Salem[b]

Department of Chemistry, College of Science, University of Basrah

[a] Corresponding author: email: *Tahseen.saki@uobasrah.edu.iq*
https://orcid.org/0000-0003-3155-5810
[b] email: *bushra.abdulaziz@uobasrah.edu.iq*
https://orcid.org/0000-0003-2370-0416

ABSTRACT

This research work deals with the preparation hydrogel based on Chitosan (CS) and Carrageenan (CG) have been studied. Polyelectrolyte complexes (PECs) hydrogels were prepared using Chitosan and Carrageenan with glutaraldehyde as the crosslinking agent. The ratio of glutaraldehyde as crosslinking agents was investigated. Upon cross-linking with glutaraldehyde was varied as 0, 20,50 and 80% (w/w) of the total quantity of chitosan and carrageenan. Prepared hydrogels were characterized for swelling ability in (pH = 1.2 acidic, 8.2 basic, 7.4 neutral), FTIR, mechanical and thermal properties. Results showed that swelling or water absorbency decreased with increased concentration of glutaraldehyde. Prepared hydrogels maintained high swelling in acidic media as compared to neutral and basic. FTIR spectroscopy indicated formation of a Schiff base C=N bond due to reaction between NH_2 of chitosan and the aldehyde group of glutaraldehyde. The mechanical properties assay findings prove that physically crosslinked chitosan/carrageenan are more biocompatible and enhance more the adhesion with addition chemical crosslinked by glutaraldehyde. The addition of glutaraldehyde improves strengthens of the chitosan/carrageenan and its thermal properties; the resulting was found to be more efficient for thermal properties than their non-crosslinking blend.

Keywords: Chitosan, Carrageenan, Hydrogel films, Mechanical Properties, Thermal properties

1. Introduction

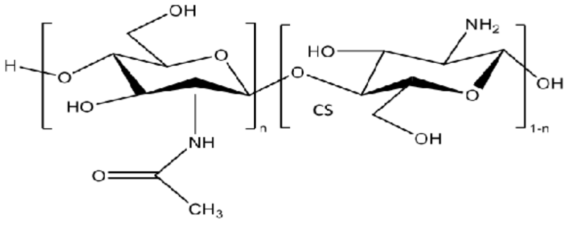
Hydrogels are cross-linked polymeric materials that can absorb large volumes of water. The Hydrogels ability to absorb water is due to hydrophilic groups in polymers chemical structure (1). Hydrogels exhibit a distinctive swelling tendency without dissolving in an aqueous environment because of their high-water absorption capacity and the presence of crosslinks in their structure (2). In hydrogel formulations, various cross-linking techniques have been employed. Hydrogel compositions often employ physical and chemical techniques. Hydrogen bonds, covalent bonds, van der Waals interactions or physical entanglements are the sources of cross-links in polymeric networks (3). Polyelectrolyte complexes (PECs) are macromolecules with a lot of charged or easily charged groups occurred when oppositely charged polyelectrolyte solutions are mixed without the need of solvents (4). PECs are being studied more and more in academia and industry because of their easy manufacture and excellent delivery system for macromolecules and pharmaceuticals that are prone to deterioration (5,6). The hydrophilic-hydrophobic balance, molar mass, charge density, ionic strength and the polyion mixing mode of the complimentary polymers, can all be used to adjust PEC properties. Secondary bonds such as van der Waals interactions and hydrogen bonds play a major role in the formation and integrity of PECs. However, pH values are important values in the formation PEC between polyelectrolytes (7). Chitosan (CS) is a naturally polysaccharide with varying molecular weights and degrees of deacetylation that are deacetylated derivatives of the natural polysaccharide chitin. It is made up of deacetylated units called β-1,4-linked glucosamine and acetylated units called N-acetyl-d-glusoamine, with molecular weights ranging from 10 to 1,000 kDa and typical deacetylation levels between 70-95% and presence of reactive functional groups, such as NH_2 and OH (8). Chitosan considers one of naturally occurring cationic polysaccharide functions well as a bioadhesive substance. Furthermore, because of its hydrophilic nature, high availability, great biocompatibility, and biodegradability, chitosan-based PECs have been widely used in drug delivery (9). PECs based on chitosan and related polymers have been utilized in medication delivery for the past few decades. Controlled release of proteins and vaccines. However, the cationic amino group at the C2 position of the repeating glucopyranose unit of chitosan can electrostatically interact with the anionic groups of other polyions to form PECs many different polyanions of natural origin such as hypromellose phthalate (10) and carboxymethyl cellulose sodium (11) Sodium alginate (12) alginate, carrageenan (13). Carrageenan (CG) is an anionic polymer naturally occurring, high molecular weight biopolymer that is ecofriendly and non-irritating, allowing for its usage in biomedical applications. CG has alternating α(1-3)-D-galactose-4-sulfated and β(1-4)-3,6-anhydro-D-galactose units, containing one sulfate group per disaccharide unit (14). However, the scientific papers and application of using glutaraldehyde to synthesis a crosslinked chitosan/carrageenan is little (15-17). Therefore, this article using glutaraldehyde as a crosslinking agent to create a novel resin material based on chitosan/carrageenan chitosan hydrogel.

Chitosan/Carrageenan (CS/CG) hydrogel blend were prepared by PECs of oppositely charged CS (cation) and CG (anion). Also, prepared CS/CG hydrogel blend with glutaraldehyde as the cross-linking agent.

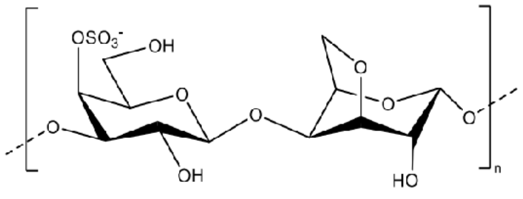
2. Materials and Method

2.1. Chemicals

Chitosan (CS) 75% (CAS Number 9012-76-4) from HIMEDIA, Carrageenan (CG) (CAS Number 9000-07-1) from SIGMA-ALDRICH. Glycerol from Fluka, gluteraldehyde and acetic acid from PDH.



Chitosan (CS)



Carrageenan (CG)

2.2. Preparation Polyelectrolyte Complexes

Bio-polymeric films were prepared by dissolving each of polymers separately, where1g of CS was dissolved in 1% acetic acid with continuous stirring (500 rpm) for 15 minutes, then leave it for 15 minutes until the bubbles disappear.

CG was dissolved by distilled water with continuous stirring. After that, added drop by drop to CS by stirring to obtain a homogeneous solution. Before the last addition, 0.1 ml of glycerol was added to give elasticity to the prepared films.
Three ratios were used 20, 50, and 80% of the crosslinking agent, gluteraldehyde was added to the total solution. The homogenized solution was transferred to a Petri dish and allowed to dry at laboratory temperature. After drying, the films were washed with distilled water to get rid of the acid.

2.3. Swelling index

Swelling indicators were recorded for the prepared polymeric films (PECs) by immersing samples of similar weight in different acidic solutions (pH) (1.2, 7, 8.2) at room temperature. Then removing them from the solutions at regular time intervals and recording the weight of the sample after drying it. For each entanglement rate, three samples were taken and immersed in the media mentioned above. The swell ability was determined by the following equation:

$$Q\% = W_s - W_d / W_d * 100$$

Q represents the swelling ratio, W_s represents the weight of the swollen film, W_d represent the weight of the dry film.

3. Results and Discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra obtained for the Chitosan/Carrageenan hydrogels containing 80% glutaraldehyde (cross-linking agent) are collected together for better comparison are shown in Figure 3. The peaks at 1648 to amide I ($CONH_2$) and 1545 cm^{-1} corresponded to amide II (NH_2) was dedicated in the chitosan spectrum (Figure 1). In the spectrum ((Figure 2) of the carrageenan, the peak at 1221 cm^{-1} was belonging to the band of S=O (SO_4). In comparison, the FTIR spectrum (Figure 3) of the Chitosan/Carrageenan cross-linked with glutaraldehyde (80%) showed a decrease in peak intensity of $–NH_3^+$ of chitosan at 1450 cm^{-1} and appeared a new peak at 1699 cm^{-1} indicated the formation of linkage (C=N imine) from reaction NH_2 groups of chitosan and the C=O groups of glutaraldehyde.

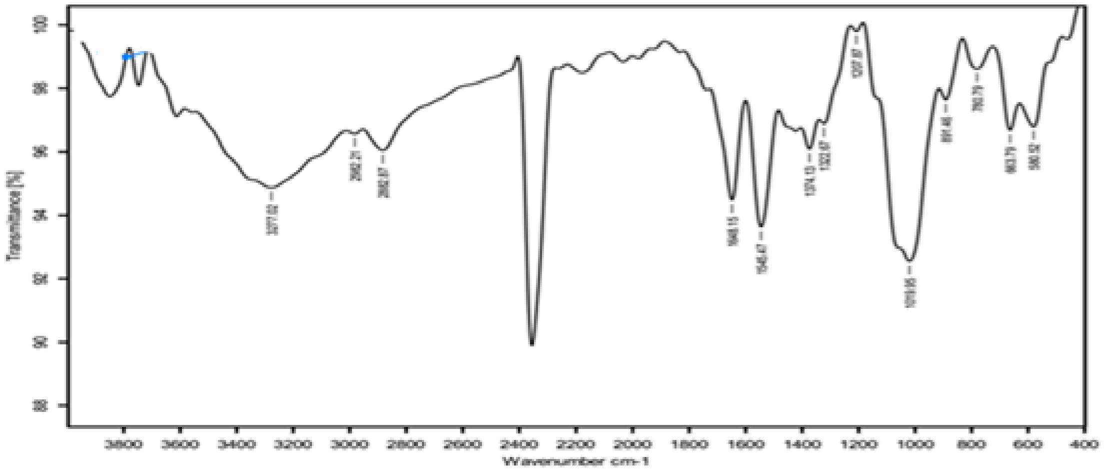


Figure 1. FTIR spectroscopy of the Chitosan

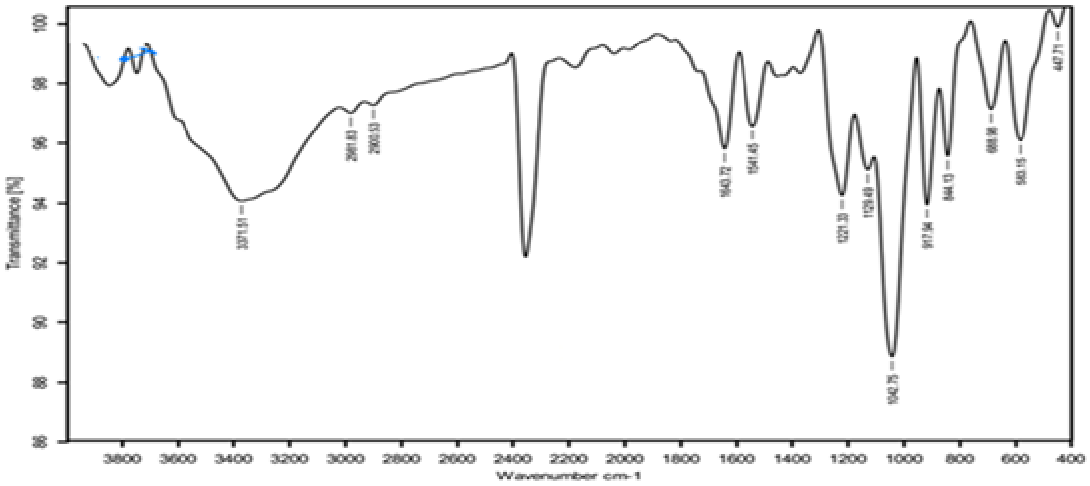


Figure 2. FTIR spectroscopy of the Carrageenan

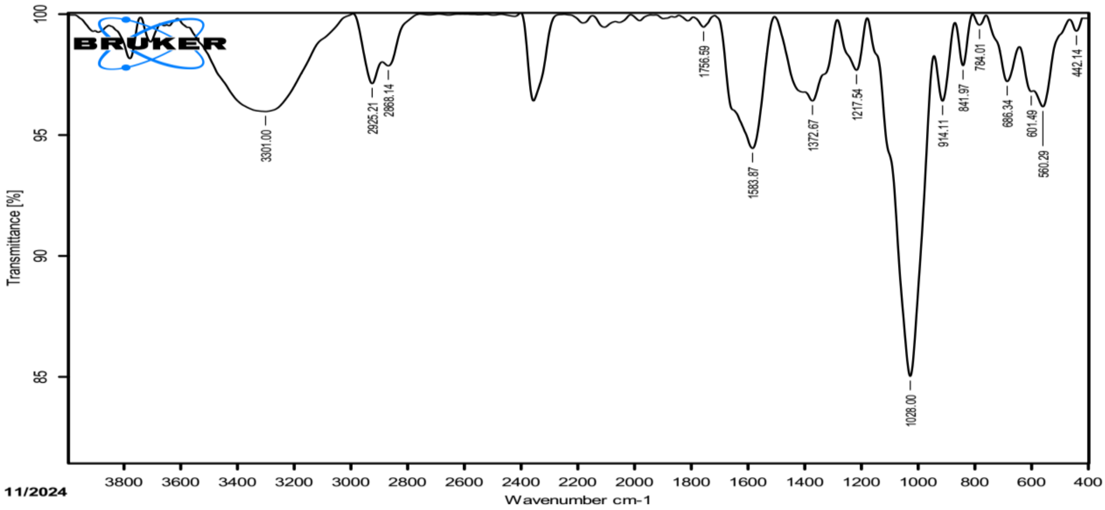


Figure 3. FTIR spectroscopy of the CS/CG/glutaraldehyde

3.2. Swelling Study

The swelling ratio study of the CS/CG was performed in 3 dissolution systems by the pH media 1.2; 7.4 and 8.2. The hydrogel blend prepared without any addition of crosslinking agent had highest swelling ratio. However, swelling ratio of the blend decreased with increased addition of crosslinking agent (glutaraldehyde). On the other hand, the highest value of swelling was detected in acidic pH media. Polymeric chains of chitosan and carrageenan had complete freedom of movement, when was not added with crosslinking agent. In other words, increasing the crosslinker concentration forms a strong structure that reduce the swelling due to decrease in the movement of the polymer chains besides decreased the number of hydrophilic groups present in them, lower their ability to absorb water, see Figure 4.

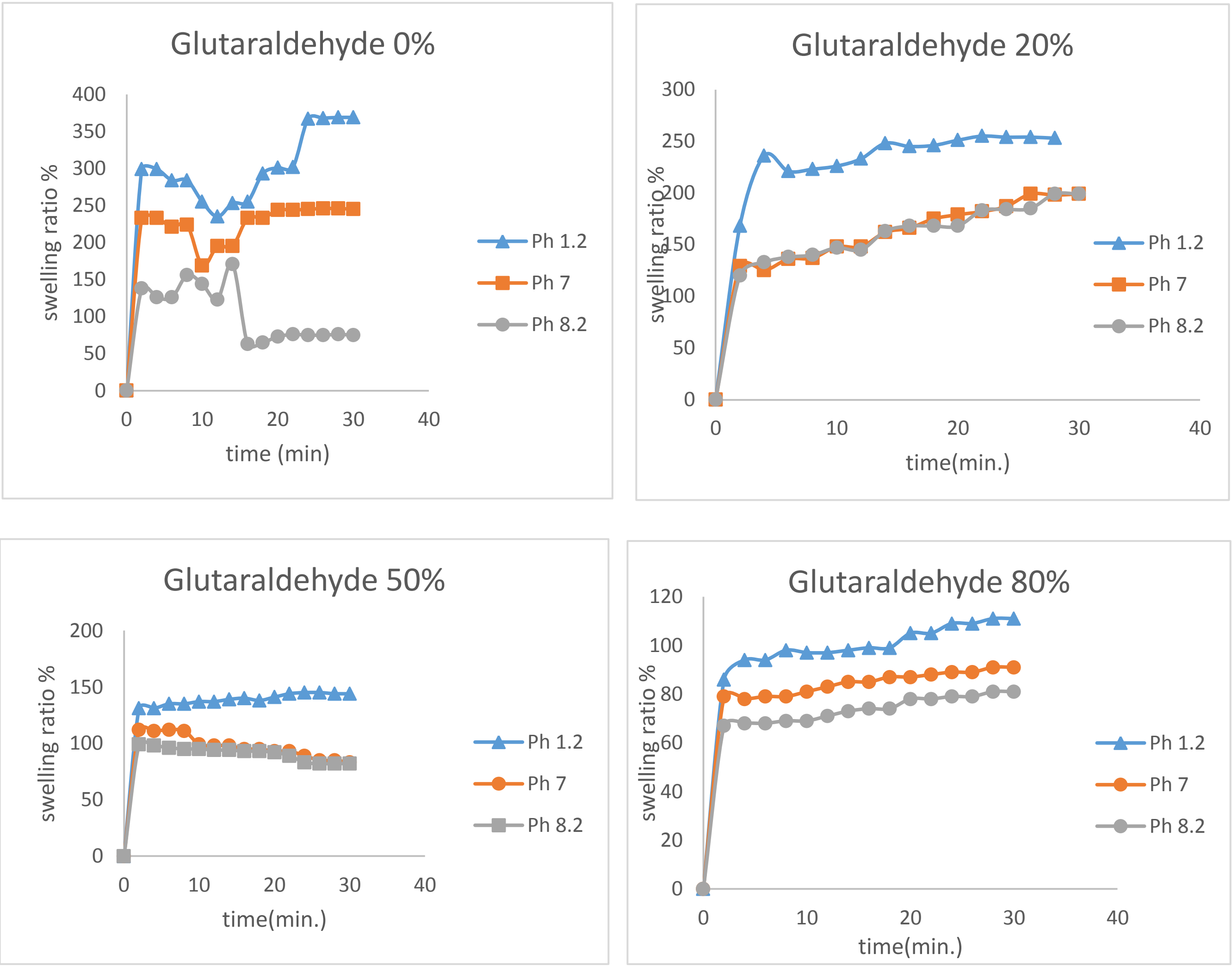


Figure 4. Swelling ratio obtained for the prepared Chitosan/Carrageenan blend hydrogels

3.3. Mechanical Properties

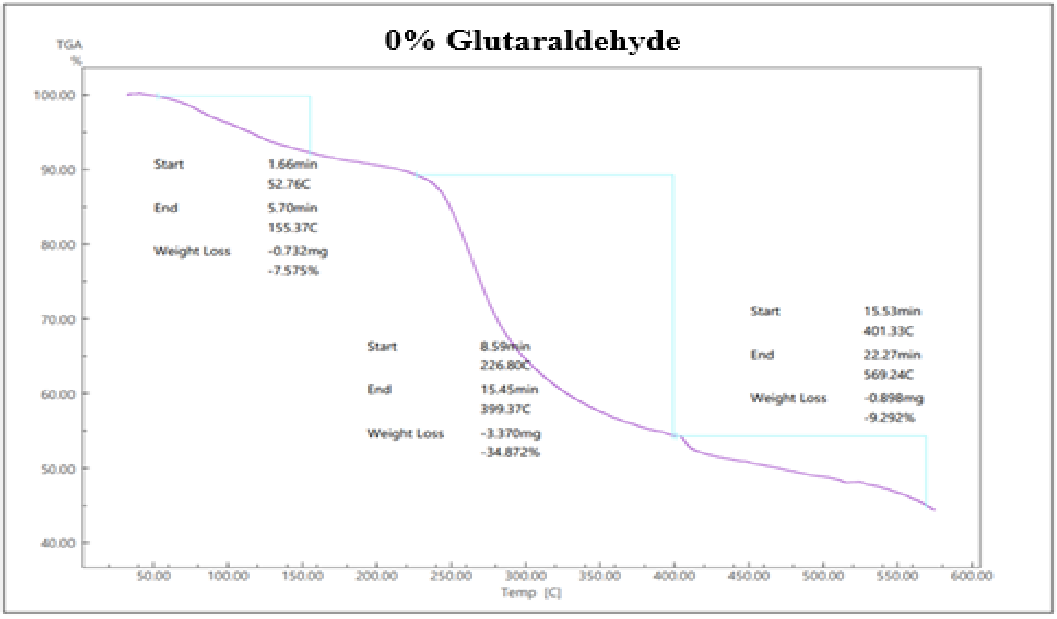
As shown in Table 1 the CS/CG gel films showed good mechanical properties, with δ_B, ε_B, and E being results superior to the values of CS/CG gel without crosslinking agent (glutaraldehyde). As expected, weight ratio of glutaraldehyde significantly influenced the mechanical performance of the gels. The gel film with a weight ratio 80% had the maximum δ_B and δ_M, whereas the CS/CG gel film with a weight ratio 50% possessed the lowest values. However, it was interesting that the CS/CG with slight excess of glutaraldehyde had the highest values of mechanical properties data. Crosslinking bridge bonds formed when added glutaraldehyde, resulting in a rigid and brittle physical CS/CG gel. It was remarkable that the CS/CG gel possessed good mechanical performances over a wide range of weight ratio. This characteristic occurred due to multiple interactions and the crosslinking network of the gels (7).

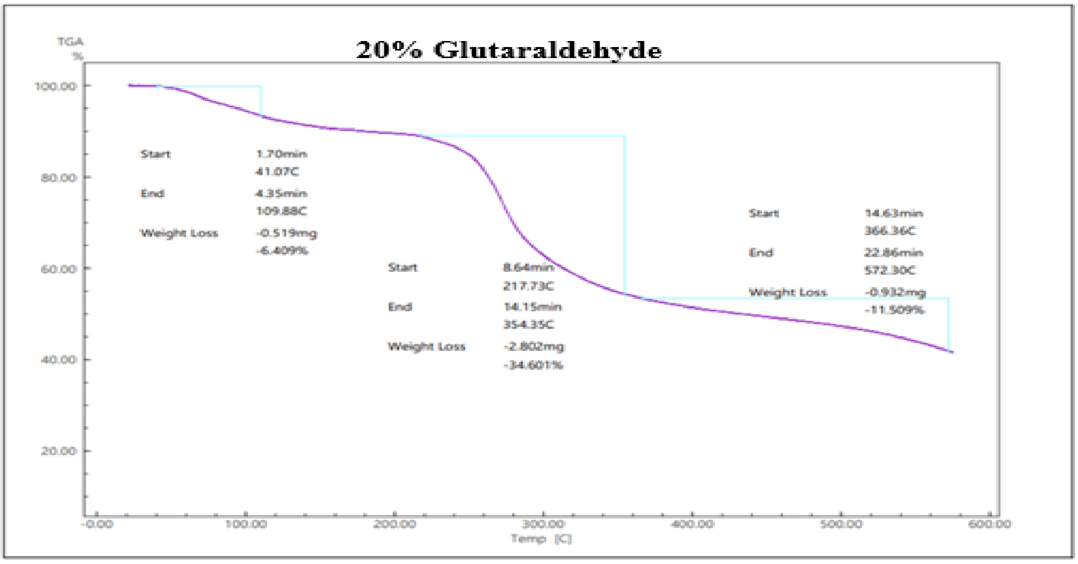
Table.1. Mechanical properties data of the Chitosan/Carrageenan blend with different ratio of glutaraldehyde

Glutaraldehyde Ratio %	**δ_M (Mpa)**	**ε_M %**	**δ_B(Mpa)**	**ε_B %**	**Young Modulus E (Mpa)**
0	5.48	1.0	5.46	1.0	5.48
20	7.32	0.9	7.32	0.9	8.13
50	2.73	0.6	2.6	0.7	4.55
80	10.1	1.1	9.6	1.1	9.18

3.4. Thermogravimetric analysis TGA

Thermo gravimetric analysis TGA was measure the thermal stability of the CS/CG blends with different percentages of glutaraldehyde with heating rate 20 ^{o}C.min^{-1} in inert atmosphere (Figure 5). The weight losses at different temperatures were analyzed. It is obvious, that the weight loss (%) of CS/CG blends crosslinked glutaraldehyde was greater compared to that of blends without crosslinking agent. Ultimate degradation temperature of blends without glutaraldehyde is 265 ^{o}C. However, added glutaraldehyde to the blends in several % ratio, which enhance the thermal stability compared with non-crosslinking blend. However, degradation temperature of blend cross-linked with 20, 70 and 80% glutaraldehyde were at 267, 269 and 280 ^{o}C respectively. Also, from the char content results we are able to conclude that the prepared CS/CG blends showed relatively high thermal stability as shown in Table 2.





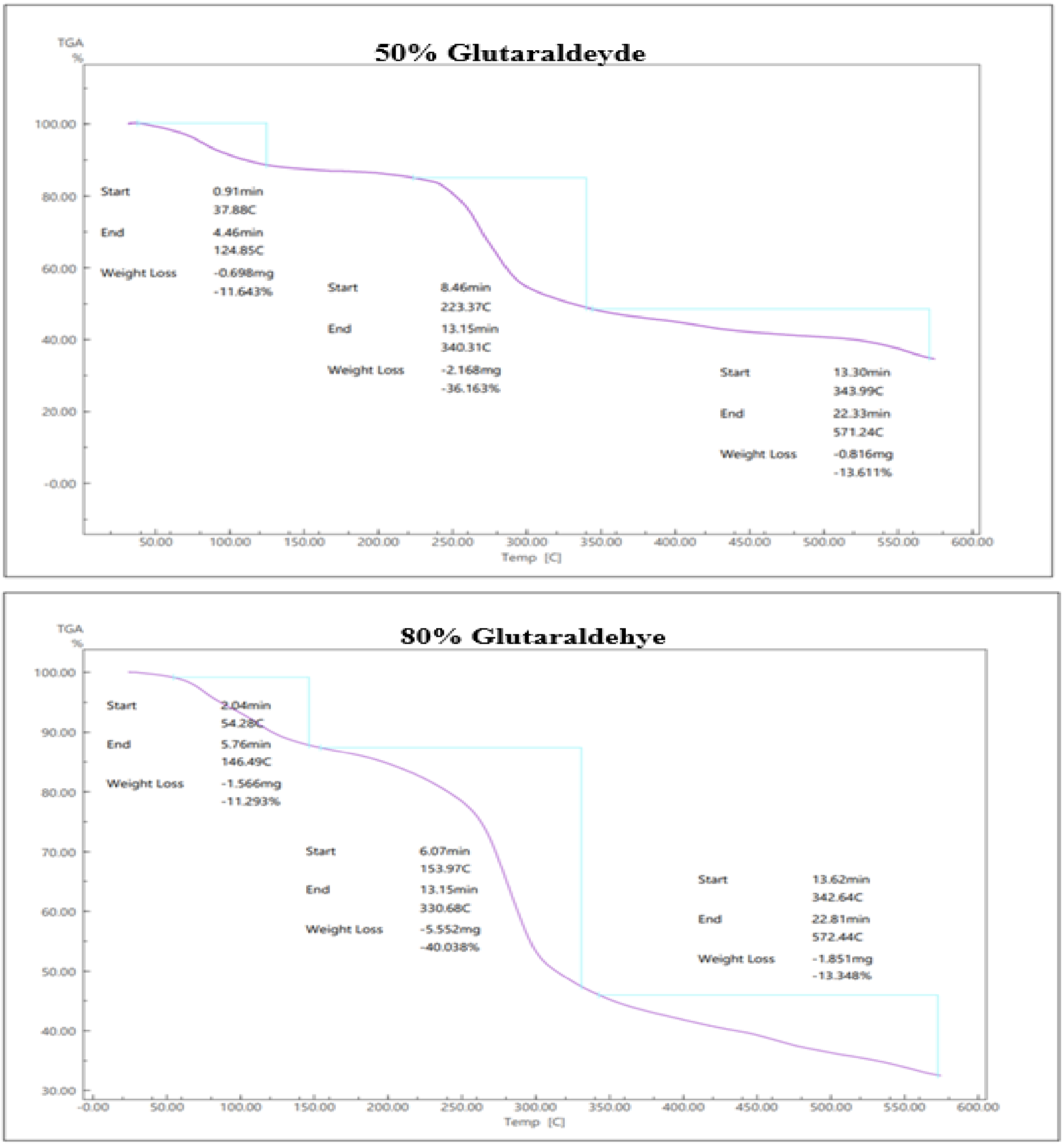


Figure 5. Thermogravimetric analysis curves of CS/CG blends with different ratio of Glutaraldehyde

Table.2. Thermal properties data of the CS/CG blend with different ratio of Glutaraldehyde

Glutaraldehyde Ratio %	Ultimate Decomposition Temperature °C	Weight Loss%	Temperature of Weight Loss °C	Rate of Decomposition (min^{-1}. %)	Char %Content At 550 °C
0	265	25	275	1.5	48.26
		50	485		
		75	-		
20	267	25	292	1.54	51.3
		50	488		
		75	-		
50	269	25	270	1.36	38.5
		50	330		
		75	-		
80	280	25	268	1.41	35.32
		50	310		
		75	-		

4. Conclusion

A series of hydrogel blends were prepared using chitosan and carrageenan with glutaraldehyde as the crosslinking agent. Prepared hydrogels were characterized for water absorbency or swelling ability in acidic and basic pH and neutral media, FTIR spectroscopy, mechanical and thermal properties. It was found that swelling capacity decreased with increased concentration of glutaraldehyde in the blends. However, prepared hydrogel had higher water absorbency in acidic media as compared to basic and neutral PH. Prepared hydrogels exhibited good mechanical properties and thermal stability.

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