PREPARATION AND ANALYSIS OF NOVEL Hydrogels Prepared from the Blend of Guar Gum and Chitosan: Cross-linked with Glutaraldehyde

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ABSTRACT

This research work deals with the preparation of a series of hydrogels using renewable resources, in order to decrease the adverse impact on the environment, and understand their swelling behavior. Hydrogels were synthesized using guar gum and chitosan with glutaraldehyde as the cross-linking agent, protonated with 98% conc. sulphuric acid. Concentration of chitosan was varied as 0, 12.5, 25, 37.5 and 50% (w/w) in guar gum, while that of glutaraldehyde was varied as 0, 1.5, 3 and 6% (w/w) of the total quantity of guar gum and chitosan. Prepared hydrogels were characterized for moisture content, equilibrium water absorbency, re-swelling capacity, swelling ability in acidic (pH = 3) and basic (pH = 11) pH distilled water, equilibrium saline water absorbency and Fourier transform infrared spectroscopy. It was determined that moisture content, equilibrium water absorbency and equilibrium saline water absorbency decreased with increased concentration of chitosan and glutaraldehyde, but they still had water swelling to be classified as hydrogel. Re-swelling capacity of the hydrogels decreased with increased cycles of reswelling. Prepared hydrogels maintained high water swelling in acidic pH distilled water as compared to basic pH distilled water. This hydrogels can be utilized as eco-friendly water manageable materials.

Keywords

guar gum, chitosan, glutaraldehyde, sulphuric acid, re-swelling

1. INTRODUCTION

Hydrogels are hydrophilic materials having capacity to absorb water. However, they are insoluble in water due to the presence of a three-dimensional network structure. Hydrophilicity in hydrogels is induced by the presence of hydrophilic groups, such as hydroxyl, carboxyl, amide, and sulfonic groups, along the polymer chain; whereas the cross-links are formed by either covalent bonds, electrostatic or dipole–dipole interactions. Hydrogels are cross-linked polymeric materials swelling in water to an equilibrium value. It is generally agreed that, for a material to be classified as hydrogel, it should absorb at least 10% w/w water and must be insoluble in it. [1] Materials that are largely used in making hydrogels include acrylates [2-6], acrylamides [7-10], silicone [11-14], proteins [15-18], polysaccharides [19-21] etc. Hydrogels have wide spread applications ranging from contact lenses [22, 23], drug delivery [24], tissue engineering [25], wound dressings [26], soil water retention [27] to disposable diapers [28].

Since 1970s many reports have been published in the scientific literature about new chemical and physical structures, properties and innovative applications of polymer hydrogels. However, recently many researchers are working on hydrogels prepared from biopolymers like guar gum and chitosan. Barbucci et al. [29] prepared guar gum based porous structure hydrogels by cross-

linking with polyethylene glycol diglycidyl ether; which were found to be unaffected by the pH of the solution. Ozcelik et al. [30] investigated the ultrathin chitosan - poly (ethylene glycol) based hydrogel films for corneal tissue engineering application. They observed that through variation of the poly (ethylene glycol) content it was possible to tailor the hydrogels to have tensile strains and ultimate stresses identical to or greater than those of human corneal tissue; while, retaining similar tensile moduli. Xiao et al. [31] studied the properties of the hydrogel films prepared from chitosan and hydroxypropyl guar gum; and determined improvement in tensile strength and elongation at break with increased concentration of hydroxypropyl guar gum in chitosan. Lim et al. [32] utilized hyaluronic acid and polyethylene glycol based hydrogel nanoparticles as effective carriers in transdermal delivery systems. They reported enhanced drug delivery efficiency in the skin with the help of this hydrogel nanoparticles. Soppimath et al. [33] synthesized a series of anionic hydrogels based on polyacrylamide grafted with guar gum to be utilized in pH sensitive drug delivery systems. Huang and Xiao [34] synthesized hydrogel membranes using cationic guar gum and poly (acrylic acid). Very strong interactions were found to have occurred between them resulting in a uniform structure and complete miscibility. Thermal stability of poly (acrylic acid) was determined to have increased with increased concentration of cationic guar gum. Wang et al. [35] synthesized a range of granular, micro-spherical hydrogels by free radical grafting mechanism using chitosan, acrylic acid, gelatin and N, N- methylene-bisacrylamide. Liu and Lin [36] investigated the properties of carboxymethyl and hexanoyl substituted chitosan based hydrogels having pH sensitivity; which was found to be dependent on the degree and nature of such substitutions. It was found that the pH sensitivity of the hydrogel was more pronounced in carboxymethyl substituted chitosan as compared to hexanoyl group substituted chitosan due to the altered state of water absorption caused by inhibiting the intermolecular hydrogen bonding. Wang et al. [37] prepared superabsorbent hydrogel composites using guar gum, acrylic acid and attapulgite clay by graft polymerization process preparing guar gum-g-poly (acrylic acid)/attapulgite; which exhibited improved water absorbing and waterretention capability, swelling rate, pH-resistant property and reusability. Sandolo et al. [38] investigated the effect of temperature (7, 15, 25 and 37 °C) on the rheological property and crosslinking density of hydrogel prepared using guar gum cross-linked with glutaraldehyde. Fujioka et al. [39] investigated the synthesis of novel superabsorbent hydrogels based on the reaction of guar gum and succinic anhydride, using 4-dimethylaminopyridine as the esterification promoter demonstrating maximum absorbency in pure water of ca. 200 g water/g dry gel.

This research work describes a study on the synthesis of series of novel hydrogels from guar gum and chitosan using glutaraldehyde as the cross-linking agent. Prepared hydrogels were characterized for degree of hydration, equilibrium water absorbency, re-swelling capability and were also investigated for understanding the effect of pH and salinity on their absorption behavior. The reaction between glutaraldehyde and the polymer – chitosan and guar gum was investigated using the Fourier transform infrared spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

Guar gum (intrinsic viscosity measured at 30 °C: 10.0 dL/g, Figure 1) was obtained from Sigma Aldrich, Mumbai, India. Chitosan (Seacure® 123, viscosity measured at 30 °C: 15 cps, Figure 1) was procured from Pronova Biopolymer A. S., Norway. Glutaraldehyde (25% w/v), acetic acid, ethylenediaminetetraacetic acid (EDTA) and 98% conc. sulphuric acid were supplied by S. D. Fine Chemicals Pvt. Ltd., Mumbai, India. All chemicals obtained from S. D. Fine Chemicals Pvt. Ltd. were of analytical grade. Distilled water was obtained from Bio Lab Diagnostics India Pvt. Ltd., Mumbai, India. All chemicals were used as obtained without any purification or modification.

2.2 Preparation of hydrogels

Hydrogels in this study were prepared as per the scheme shown in Figure 1. Prepared guar gum/chitosan hydrogel compositions and their nomenclature are listed in Table 1. Chitosan was added upto 50% (w/w) of guar gum; whereas the concentration of glutaraldehyde (cross-linking agent) was varied as 0, 1.5, 3 and 6 % (w/w, total weight of guar gum and chitosan), to prepare guar gum/chitosan blend based hydrogels.



Figure 1. Scheme of reaction between guar gum and chitosan induced by glutaraldehyde in the presence of 98% conc. sulphuric acid

In a 1L beaker, guar gum (5 g) was added in distilled water to prepare its 1% (w/v) solution and was kept under mechanical stirring for 48 h at 1500 rpm. A couple of drops of 98% concentrated sulphuric acid were then added to this solution; and was mechanical stirred for another 1 h at an rpm of 1500 at room temperature. Whereas; in another 250 ml beaker, required quantity of chitosan (depending on the composition, see Table 1) was added to 2% (v/v) acetic acid solution (2 ml in 100 ml water), to prepare 5% (w/v) chitosan solution and the mixture was stirred for 4 h at room temperature, at 1500 rpm. Chitosan is insoluble in plain distilled water, but is readily soluble in acidic solution. [40] This chitosan solution was then added in to the guar gum solution, preparing the required guar gum/chitosan blend formulation. The guar gum/chitosan mixture was added with varying amounts of glutaraldehyde (see Table 1 for compositions prepared) and stirred for another 4 h. Glutaraldehyde used was of 25% w/v solution in water. Thus, calculations of glutaraldehyde were made accordingly. The obtained gels were dried in an oven at 70 °C to obtain a constant weight, were ground and screened through a 16-mesh sieve to get granular product.

Addition of sulphuric acid protonates the aldehyde group of the glutaraldehyde making it capable to react with the –OH group of guar gum and, -OH and –NH₂ groups of chitosan, forming water molecules and covalent linkages (see Figure 1). [41] Addition of sulphuric acid directly to the chitosan solution was avoided, as sulphuric acid will spontaneously react with chitosans –NH₂ functional group. Whereas, adding it to guar gum solution, makes it enough dilute to avoid direct reaction with the –NH₂ groups of chitosan. EDTA was added as 1% of the total weight of guar gum and chitosan, acting as an anti-bacterial agent. Due to the presence of various forms of glutaraldehyde in solution (free aldehyde, mono- and dihydrated monomeric glutaraldehyde, monomeric and polymeric cyclic hemiacetals) [42, 43], it is not possible to give an exact description of the resulting network. However, tentative structure is shown in Figure 1. Nevertheless, glutaraldehyde has been frequently used as a cross-linker since it is not expensive, readily available and highly soluble in aqueous solution.

Table 1 Prepared guar gum/chitosan hydrogel compositions and their nomenclature

Sr.		Cuar gum	Chitasan	Glutaraldehyde [#]		
No	Nomenclature	Guai guin	(g)	1.5 %	3 %	6 %
•		(g)	(g)	(g)	(g)	(g)
1.	GC 100/0/0*	5.00	0.00	-	-	-
2.	GC 100/0/1.5	5.00	0.00	0.30	-	-
3.	GC 100/0/3	5.00	0.00	-	0.60	-
4.	GC 100/0/6	5.00	0.00	-	-	1.20
5.	GC 87.5/12.5/0	5.00	0.71	-	-	-
6.	GC 87.5/12.5/1.5	5.00	0.71	0.34	-	-
7.	GC 87.5/12.5/3	5.00	0.71	-	0.68	-
8.	GC 87.5/12.5/6	5.00	0.71	-	-	1.37
9.	GC 75/25/0	5.00	1.67	-	-	-
10.	GC 75/25/1.5	5.00	1.67	0.40	-	-
11.	GC 75/25/3	5.00	1.67	-	0.80	-
12.	GC 75/25/6	5.00	1.67	-	-	1.60
13.	GC 62.5/37.5/0	5.00	3.00	-	-	-
14.	GC 62.5/37.5/1.5	5.00	3.00	0.48	-	-
15.	GC 62.5/37.5/3	5.00	3.00	-	0.96	-
16.	GC 62.5/37.5/6	5.00	3.00	-	-	1.92
17.	GC 50/50/0	5.00	5.00	-	-	-
18.	GC 50/50/1.5	5.00	5.00	0.60	-	-
19.	GC 50/50/3	5.00	5.00	-	1.20	-
20.	GC 50/50/6	5.00	5.00	-	-	2.40

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* GC 100/0/0, in the alphanumeric sequence, denotes blend of guar gum (G) and chitosan (C) containing 100% guar gum (100) and 0% chitosan (0) prepared with addition of 0% (0) glutaraldehyde. Similar type of nomenclature was used for naming other samples, except there was change in the percentages of the components.

Glutaraldehyde used was of 25% w/v solution in water. Thus, calculations were made accordingly.

3. CHARACTERIZATION AND TESTING

3.1 Moisture content

0.05 g film samples were accurately weighed (w_0) and dried in an air-circulating oven for 5 h at 70°C. Samples were then removed from the oven and immediately weighed (w_1) . Weight of the films, before and after drying, was accurately weighed. All samples were analyzed in triplicate.

The moisture content was determined as the percentage of water in the films according to Equation 1.

Water content = $[(w_0 - w_1) / w_0] \ge 100$ (1)

3.2 Measurement of the equilibrium water absorbency

0.05 g of samples were immersed in excessive distilled water at room temperature for 4 h to reach the swelling equilibrium. Equilibrium swollen samples were separated from the unabsorbed distilled water using a mesh screen and were allowed to drain on the sieve for 10 min. Water absorbency of the prepared hydrogel samples was determined by weighing the swollen samples, and calculated as per the Equation 2. Water absorbency data were the average values of three measurements.

Water absorbency
$$(Q_{eq}) = (w_3 - w_2)/w_2$$
 (2)

where, Qeq is the water absorbency calculated as grams of distilled water per gram of the sample, w_2 is the weight of dry hydrogel sample and w_3 is the weight of distilled water swollen samples.

3.3 Re-swelling capability

0.05 g sample was soaked in 100 ml of distilled water at room temperature to achieve the swelling equilibrium. Swollen gel was weighed and placed in an oven at 100 °C until the gel gets thoroughly dried. Recovered hydrogel was then again immersed in another equal volume of water. The procedure was repeated and the saturated absorbency of the sample after several reswelling cycles was obtained.

3.4 Measurement of the equilibrium saline water absorbency

0.05 g of sample was immersed in 0.9 % w/v NaCl distilled water solution at room temperature for 4 h to reach the swelling equilibrium. Equilibrium swollen samples were separated from the unabsorbed saline water using a mesh screen. Screened swollen samples were allowed to drain on the sieve for 10 min. Equilibrium saline water absorbency of the prepared hydrogel samples was determined by weighing the swollen samples, and calculated as per Equation 3. Equilibrium saline water absorbency data were the average values of three measurements.

Equilibrium saline water absorbency $(S_{eq}) = (w_5 - w_4) / w_4$ (3)

where, w_4 = weight of dry sample and w_5 = weight of equilibrium saline water swollen sample

3.5 Effect of pH on the equilibrium water absorbency

This study was undertaken to understand the effect of distilled water pH on the swelling behavior of the prepared hydrogels. This test was performed in the same way as that for measuring the equilibrium water absorbency. The only difference was the pH of distilled water was maintained either acidic (pH = 3) or basic (pH = 11). Swelling data were collected as per the Equation 2.

3.6 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the guar gum/chitosan blend based hydrogel were recorded with a PerkinElmer, Spectrum GX equipment. Samples were scanned with a resolution of 2 cm^{-1} in the scan range of 450–4000 cm⁻¹.

4. RESULTS AND DISCUSSION

Structurally, chitosan is different from guar gum only because of the replacement of certain of the hydroxyl groups by the amine groups. Thus, technically, the total number of functional group present on chitosan and guar gum remains same. Glutaraldehyde was added taking into consideration the total weight of guar gum and chitosan. Thus, there will not be any difference in the reactivity of the glutaraldehyde towards them and also the number of cross-links that can get formed with chitosan and guar gum would be ideally same. Amines are generally more reactive than hydroxyls, but this will not be of concern in our situation. The reaction of guar gum and chitosan with glutaraldehyde is happening in the solvent media, (water) in which both of them are diluted to 1% solution. Thus, the solution is enough dilute to negate the effect of amines high reactivity as compared to hydroxyl groups. Therefore, the probability of them undergoing reaction with glutaraldehyde is same. Thus, replacing certain amount of guar gum by chitosan must not affect the level of cross-linking.

4.1 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra obtained for the prepared hydrogels are shown in Figure 2. Hydrogels containing no cross-linking agent (glutaraldehyde) and the ones containing 6% cross-linking agent are clubbed together for better comparison. In Figure 2, A-E refer to the FTIR spectra obtained for GC 100/0, GC 87.5/12.5, GC 75/25, GC 62.5/37.5 and GC 75/25 respectively, cross-linked with 0% and 6% glutaraldehyde.

Broad band at 3600 cm^{-1} is attributed to the stretching vibration of the –OH groups present due to water molecules. Sharp absorption peak at 1630 cm^{-1} is due to the bending vibration of –OH groups present on guar gum and chitosan. These peaks disappeared or decreased in intensity on reacting with protonated glutaraldehyde giving rise to new peak at about 1555 cm⁻¹ belonging to the ester linkage. Whereas, the peaks at 2880, 1650, 1326 and 1080 are due to the stretching vibrations of aliphatic C-H, amine (-NH₂), amide II and amide III respectively. These are the characteristics peaks for chitosan. Intensity of this peaks also decreased on addition of glutaraldehyde (cross-linking agent), which on protonation with conc. sulphuric underwent reaction with them forming a cross-linked structure. Absorption peak at 1630 cm⁻¹ is assigned to the C=O stretching of the amide linkage. Thus, it can be confirmed that guar gum and chitosan reacted with glutaraldehyde (on its protonation with sulphuric acid) to form a cross-linked structure. Similar changes in the FTIR spectra are reported by Huang et al. [34] for hydrogel membranes prepared by its cross-linking with acrylic acid.

4.2 Moisture content

Moisture content values obtained for the prepared hydrogels is plotted in Figure 3. It is a plot of moisture content vs concentration of glutaraldehyde for various blend composition of guar gum and chitosan. It was found that the moisture content of the hydrogel decreased with increase in chitosan content in guar gum; and also with increase in concentration of glutaraldehyde. Pristine guar gum, containing no chitosan or glutaraldehyde, was determined to have moisture content of about 12.8%, which is attributed to its highly hydrophilic nature.



Figure 2. FTIR spectra obtained for the prepared guar gum/chitosan blend hydrogels

Guar gum is more hydrophilic compared to chitosan. Secondly, chitosan is not soluble in plain distilled water, but requires acidic or basic media (preferably acidic) to bring about its dissolution. Thus, chitosan absorbs less amount of moisture as compared to guar gum. Therefore, the addition

of chitosan into guar gum decreased its hydrophilicity, leading to decrease in its moisture content. Thus, moisture content of guar gum decreased with increased concentration of chitosan.



Figure 3. Effect of glutaraldehyde and chitosan concentration on the moisture content of guar gum

Glutaraldehyde was used as a cross-linking agent in the guar gum/chitosan blend hydrogel system. It was protonated with the conc. sulphuric acid to make it able to react with the -OH and -NH₂ groups present on guar gum and chitosan respectively. Hydrogel systems prepared without any addition of glutaraldehyde had highest moisture content; whereas, moisture content of the blend system decreased with increased addition of glutaraldehyde. Polymeric chains of guar gum and chitosan had complete freedom of movement, when was not added with glutaraldehyde, as the three dimensional network structure was not formed in them. This made their hydrophilic parts exposed to atmospheric moisture, absorbing moisture. In addition, the mobility and higher inter-chain gaps allowed them to accommodate water molecules from the atmosphere. However, on addition of glutaraldehyde, the functional groups (-OH and -NH₂) in the guar gum/chitosan blend system underwent reaction with each other forming a three dimensional cross-linked network structure. This led to decrease in the mobility of the polymer chains as well as decreased the number of hydrophilic groups present in them, decreasing their values of moisture content. Higher the concentration of glutaraldehyde, higher was the level of cross-linking density and thus lower was their ability to absorb moisture. Similar trend in the values of moisture content was observed by Fujioka et al. [39] in the superabsorbent hydrogels prepared using guar gum and succinic anhydride. Even Wang et al. [37] reported similar moisture content behavior for the hydrogels prepared using natural guar gum and attapulgite.

4.3 Measurement of the equilibrium water absorbency

Figure 4 represents the equilibrium water absorbency (g/g) values obtained for the prepared guar gum/chitosan blend hydrogel samples. It was found that equilibrium water absorbency decreased with increase in concentration of chitosan in guar gum. This, trend was observed regardless of addition of glutaraldehyde. However, equilibrium water absorbency decreased with increased concentration of glutaraldehyde in any of the guar gum/chitosan blend compositions. As expected, the rate of decrease of equilibrium water absorbency with increase in concentration of

glutaraldehyde is appreciable compared to that obtained through addition of chitosan. However, at higher concentration of glutaraldehyde, equilibrium water absorbency decreases to such an extent that the guar gum/chitosan blend is no more able to act as hydrogel. Whereas, hydrogel samples prepared without any or very low concentration of glutaraldehyde got dissolved in the equilibrium water absorbency test. Thus, glutaraldehyde is required in minimum of 1.5 wt% concentration so that the three-dimensional structure of the hydrogel remains and can demonstrate equilibrium water absorbency property.



🔶 0% Glutaraldehyde 📲 1.5% Glutaraldehyde 📥 3% Glutaraldehyde 😽 6% Glutaraldehyde

Figure 4. Equilibrium water swelling absorbency obtained for the prepared guar gum/chitosan blend based hydrogels

Addition of chitosan in guar gum decreased the hydrophilic nature of guar gum, as chitosan required acidic or basic medium to absorb moisture. Thus, the water resistance ability of the blend increased with increased addition of chitosan it, decreasing the equilibrium water absorbency of the blend. Protonated glutaraldehyde induced cross-linking in the blend of guar gum and chitosan by reacting with the -OH and $-NH_2$ groups present on the polymer chains. This decreased the mobility ability of these polymeric chains and also decreased the number of functional groups available to absorb water, making them less accommodative for the water absorbed. Higher concentration of glutaraldehyde leads to higher degree of cross-linking, making the polymer chains come closer to each, further decreasing their ability to absorb water. This makes them unable to swell to the extent as possible with less or no addition of glutaraldehyde. Similar effects were observed by Wen-Bo et al. [37] for GG based hydrogels grafted with acrylic acid and added with attapulgite clay, and carboxymethyl chitosan-g-polyacrylic acid by Yu and Tan [44]. Interestingly, at high concentration of glutaraldehyde (3 and 6 wt%), due to the excessive cross-linking than required, the chain mobility of guar gum and chitosan decreases to such an extent that they are no more able to act as hydrogel. Fujioka et al. [39] demonstrated near about same equilibrium water absorbency as that of ours for 4 h immersed samples.

Thus, it can be said that 1.5 wt% addition of glutaraldehyde is sufficient to obtain hydrogels from guar gum and chitosan, with better equilibrium water absorbency without bringing about their dissolution; whereas, chitosan only marginally affects the equilibrium water absorbency of the guar gum.

4.4 Re-swelling capability

After a thorough dewatering of the swollen guar gum/chitosan blend hydrogels, the resulting dry polymer blend system still showed better equilibrium water absorbency. Equilibrium water absorbency values obtained for the prepared hydrogels after 1st, 2nd and 3rd swelling are shown in Figure 5. It was found that hydrogel samples containing no or less amount of chitosan and without or very less amount of glutaraldehyde (i.e. 1.5%) got dissolved in the distilled water; however, swelling decreased for hydrogel samples containing higher content of chitosan and glutaraldehyde. Re-swelling capacity decreased with increased re-swelling, probably due to the degradation of the polymer matrix (guar gum and chitosan) while drying in oven at 100 °C.



Figure 5. Re-swelling capacity obtained for the prepared guar gum/chitosan blend based hydrogels

These results demonstrate that the addition of chitosan and glutaraldehyde is helpful for improving the reusability of the hydrogel, as the samples didn't get dissolved. Thus, the guar gum/chitosan blend hydrogels containing higher content of chitosan are reusable and recyclable water absorbing materials, which can be used as a potential water-managing material.

4.5 Measurement of the equilibrium saline water absorbency

Figure 6 represents the equilibrium saline water absorbency values obtained for the prepared guar gum/chitosan blend hydrogels. Samples containing less (1.5%) or no glutaraldehyde and less or no amount of chitosan underwent dissolution in the saline water. equilibrium saline water absorbency decreased with increase in content of chitosan in guar gum/chitosan blend hydrogels. Addition of glutaraldehyde (cross-linking agent) decreased the equilibrium saline water absorbency of the blend hydrogel.



Figure 6. Equilibrium saline water swelling absorbency obtained for the prepared guar gum/chitosan blend based hydrogels

Chitosan absorbs water only in acidic or basic condition. As, such chitosan is nearly insoluble in water. On the other hand, one can say that chitosan absorbs negligible quantity of water. Saline water was prepared by adding 0.9% (w/v) of NaCl in distilled water. NaCl is neutral in nature. Thus, the addition of NaCl does not change the pH of the solution. Addition of chitosan, consequently decreased the hydrophilicity of guar gum (guar gum is highly hydrophilic compared to chitosan). Therefore, the equilibrium saline water absorbency of the hydrogel decreased with increased content of chitosan. Glutaraldehyde is used in cross-linking the guar gum and chitosan together with each other to form a three dimensional network structure. Higher the concentration of glutaraldehyde, higher will be the cross-linking density, thus more strongly the polymer chains will be bonded to each other leading to the formation of three-dimensional network structure. This three dimensional network structure increased with increased concentration of glutaraldehyde, increasing the cross-linking density of the material. Moreover, higher is the cross-linking density, lower is the equilibrium saline water absorbency of the material. Thus, equilibrium saline water absorbency decreased with increased concentration of glutaraldehyde.

4.6 Effect of pH on the equilibrium water absorbency

Figure 7 shows the effect of distilled water pH on the swelling behavior of the guar gum/chitosan blends hydrogels.

From the data it can be seen that most of the hydrogel samples made using 0% and 1.5% glutaraldehyde got dissolved in the distilled water with neutral, acidic or basic pH. This is in correlation with the equilibrium water absorbency study. However, there is one interesting phenomenon happening here, which gives an idea about the effect of pH on the swelling behavior of the hydrogel samples. Nearly all samples got dissolved in acidic pH (pH = 3) distilled water, except the one containing highest quantity of chitosan; whereas, the water absorbency as well the number of samples getting dissolved were less for basic pH (pH = 11) distilled water. This shows that acidity has appreciable effect on the swelling behavior compared to basicity. Chitosan is more soluble in acidic condition as compared to basic condition. Similar type of phenomenon was observed for glutaraldehyde cross-linked guar gum/chitosan blend hydrogel samples. However,

the samples didn't get dissolved because of the three-dimensional network formed. As observed earlier, equilibrium water absorbency decreased with increased concentration of glutaraldehyde, but it was higher in acidic pH distilled water as compared to basic pH distilled water. On decreasing the pH of the solution to 3, the ionization degree of the polymer chains increased, which induced an increase in the osmotic swelling pressure between the hydrophilic network and the acidic distilled water solution. This led to expansion of the gap between the polymer chains making it able to hold more water. On the other hand, increase in the pH of the distilled water to 11 increased the ionic strength of the swelling media causing a decrease of ion osmotic pressure reducing the equilibrium swelling ability of the hydrogels.



Figure 7. Effect of pH on the equilibrium saline water swelling absorbency obtained for the prepared guar gum/chitosan blend based hydrogels

5. CONCLUSION

A series of hydrogels were successfully prepared using guar gum and chitosan using glutaraldehyde as the cross-linking agent, protonated with sulphuric acid. Prepared hydrogels were characterized for moisture content, equilibrium water absorbency, re-swelling capacity, swelling ability in acidic and basic pH distilled water, equilibrium saline water absorbency and Fourier transform infrared spectroscopy. It was found that moisture content, equilibrium water absorbency decreased with increased concentration of chitosan and glutaraldehyde in the guar gum. However, prepared hydrogel samples had higher equilibrium water absorbency in acidic condition as compared to basic condition. Prepared hydrogels can be successfully utilized in water managing applications.

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REFERENCES

- Hyon, S. H., Cha, W. I., & Ikada, Y. (1989) "Preparation of transparent poly (vinyl alcohol) hydrogel." *Polymer bulletin*, Vol. 22, No. 2, pp 119-122.
- [2] Dalton, P. D., Flynn, L., & Shoichet, M. S. (2002) "Manufacture of poly (2-hydroxyethyl methacrylate-co-methyl methacrylate) hydrogel tubes for use as nerve guidance channels" *Biomaterials*, Vol. 23, No. 18, pp 3843-3851.
- [3] Marek, S. R., & Peppas, N. A. (2013) "Insulin release dynamics from poly (diethylaminoethyl methacrylate) hydrogel systems." *AIChE Journal*, Vol. 59, No. 10, pp 3578-3585.
- [4] Magalhaes, J., Sousa, R. A., Mano, J. F., Reis, R. L., Blanco, F. J., & Román, J. S. (2013) "Synthesis and characterization of sensitive hydrogels based on semi-interpenetrated networks of poly [2-ethyl-(2-pyrrolidone) methacrylate] and hyaluronic acid." *Journal of Biomedical Materials Research Part A*, Vol. 101, No. 1, pp 157-166.
- [5] Paterson, S. M., Casadio, Y. S., Brown, D. H., Shaw, J. A., Chirila, T. V., & Baker, M. V. (2013) "Laser scanning confocal microscopy versus scanning electron microscopy for characterization of polymer morphology: Sample preparation drastically distorts morphologies of poly (2-hydroxyethyl methacrylate)-based hydrogels." *Journal of Applied Polymer Science*, Vol. 127, No. 6, pp 4296-4304.
- [6] Raafat, A. I., Araby, E., & Lotfy, S. (2012) "Enhancement of fibrinolytic enzyme production from< i> Bacillus subtilis</i> via immobilization process onto radiation synthesized starch/dimethylaminoethyl methacrylate hydrogel." *Carbohydrate Polymers*, Vol. 87, No. 2, pp 1369-1374.
- [7] Deshmukh, S., Mooney, D. A., & MacElroy, J. M. D. (2011) "Molecular simulation study of the effect of cross-linker on the properties of poly (N-isopropyl acrylamide) hydrogel." *Molecular Simulation*, Vol. 37, No. 10, pp 846-854.
- [8] Gad, Y. H., Aly, R. O., & Abdel-Aal, S. E. (2011) "Synthesis and characterization of Na-alginate/acrylamide hydrogel and its application in dye removal." *Journal of applied polymer science*, Vol. 120, No. 4, pp 1899-1906.
- [9] Zhang, X., Zheng, S., Lin, Z., & Zhang, J. (2012) "Removal of Basic Fuchsin Dye by Adsorption Onto Polyacrylamide/Laponite Nanocomposite Hydrogels." Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, Vol. 42, No. 9, pp 1273-1277.
- [10] Lu, C. H., Qi, X. J., Orbach, R., Yang, H. H., Mironi-Harpaz, I., Seliktar, D., & Willner, I. (2013) "Switchable catalytic acrylamide hydrogels cross-linked by hemin/G-quadruplexes." *Nano letters*, Vol. 13, No. 3, pp 1298-1302.
- [11] Shimizu, T., Goda, T., Minoura, N., Takai, M., & Ishihara, K. (2010) "Super-hydrophilic silicone hydrogels with interpenetrating poly (2-methacryloyloxyethyl phosphorylcholine) networks." *Biomaterials*, Vol. 31, No. 12, pp 3274-3280.
- [12] Dumbleton, K. A., Woods, C. A., Jones, L. W., & Fonn, D. (2011) "The relationship between compliance with lens replacement and contact lens-related problems in silicone hydrogel wearers." *Contact Lens and Anterior Eye*, Vol. 34, No. 5, pp 216-222.
- [13] Dumbleton, K., Woods, C., Jones, L., Richter, D., & Fonn, D. (2010) "Comfort and vision with silicone hydrogel lenses: effect of compliance." *Optometry & Vision Science*, Vol. 87, No. 6, pp 421-425.
- [14] Willcox, M. D., Carnt, N., Diec, J., Naduvilath, T., Evans, V., Stapleton, F. & Holden, B. A. (2010) "Contact lens case contamination during daily wear of silicone hydrogels." *Optometry & Vision Science*, Vol. 87, No. 7, pp 456-464.
- [15] Williams, R. J., Hall, T. E., Glattauer, V., White, J., Pasic, P. J., Sorensen, A. B., ... & Hartley, P. G. (2011) "The< i> in vivo</i> performance of an enzyme-assisted self-assembled peptide/protein hydrogel." *Biomaterials*, Vol. 32, No. 22, pp 5304-5310.
- [16] Betz, M., Hörmansperger, J., Fuchs, T., & Kulozik, U. (2012) "Swelling behaviour, charge and mesh size of thermal protein hydrogels as influenced by pH during gelation." *Soft Matter*, Vol. 8, No. 8, pp 2477-2485.
- [17] Yu, L., & Gu, L. (2009) "Hydrolyzed polyacrylonitrile-blend-soy protein hydrogel fibers: a study of structure and dynamic pH response." *Polymer International*, Vol. 58, No. 1, pp 66-73.

- [18] Lin, H., Sritham, E., Lim, S., Cui, Y., & Gunasekaran, S. (2010) "Synthesis and characterization of pH-and salt-sensitive hydrogel based on chemically modified poultry feather protein isolate." *Journal of applied polymer science*, Vol. 116, No. 1, pp 602-609.
- [19] Laroui, H., Dalmasso, G., Nguyen, H. T. T., Yan, Y., Sitaraman, S. V., & Merlin, D. (2010) "Drug-loaded nanoparticles targeted to the colon with polysaccharide hydrogel reduce colitis in a mouse model." *Gastroenterology*, Vol. 138, No. 3, pp 843-853.
- [20] Li, X., Weng, Y., Kong, X., Zhang, B., Li, M., Diao, K. & Chen, H. (2012) "A covalently crosslinked polysaccharide hydrogel for potential applications in drug delivery and tissue engineering." *Journal of Materials Science: Materials in Medicine*, Vol. 23, No. 12, pp 2857-2865.
- [21] Kim, S. H., & Chu, C. C. (2009) "Fabrication of a biodegradable polysaccharide hydrogel with riboflavin, vitamin B2, as a photo-initiator and L-arginine as coinitiator upon UV irradiation." *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, Vol. 91, No. 1, pp 390-400.
- [22] Zhang, R., Huang, Z., Xue, M., Yang, J., & Tan, T. (2011) "Detailed characterization of an injectable hyaluronic acid-polyaspartylhydrazide hydrogel for protein delivery." *Carbohydrate Polymers*, Vol. 85, No. 4, pp 717-725.
- [23] Walther, H., Lorentz, H., Kay, L., Heynen, M., & Jones, L. (2011) "The effect of < i> in vitro</i> lipid concentration on lipid deposition on silicone hydrogeland conventional hydrogel contact lens materials." *Contact Lens and Anterior Eye*, Vol. 34, No. S21.
- [24] Qiu, Y., & Park, K. (2001) "Environment-sensitive hydrogels for drug delivery." Advanced drug delivery reviews, Vol. 53, No. 3, pp 321-339.
- [25] Hoffman, A. S. (2002) "Hydrogels for biomedical applications." Advanced drug delivery reviews, Vol. 54, No. 1, pp 3-12.
- [26] Lu, G., Ling, K., Zhao, P., Xu, Z., Deng, C., Zheng, H., Huang, J., & Chen, J. (2010) "A novel in situ-formed hydrogel wound dressing by the photocross-linking of a chitosan derivative." Wound repair and regeneration, Vol. 18, No. 1, pp 70-79.
- [27] Wei, Y., & Durian, D. J. (2013) "Effect of hydrogel particle additives on water-accessible pore structure of sandy soils: A custom pressure plate apparatus and capillary bundle model." *Physical Review E*, Vol. 87, No. 5, pp 053013.
- [28] Colón, J., Ruggieri, L., Sánchez, A., González, A., & Puig, I. (2011) "Possibilities of composting disposable diapers with municipal solid wastes." *Waste Management & Research*, Vol. 29, No. 3, pp 249-259.
- [29] Barbucci, R., Pasqui, D., Favaloro, R., & Panariello, G. (2008) "A thixotropic hydrogel from chemically cross-linked guar gum: Synthesis, characterization and rheological behaviour." *Carbohydrate research*, Vol. 343, No. 18, pp 3058-3065.
- [30] Ozcelik, B., Brown, K. D., Blencowe, A., Daniell, M., Stevens, G. W., & Qiao, G. G. (2013) "Ultrathin chitosan-poly (ethylene glycol) hydrogel films for corneal tissue engineering." *Acta biomaterialia*, Vol. 9, No. 5, pp 6594-6605.
- [31] Xiao, C., Zhang, J., Zhang, Z., & Zhang, L. (2003) "Study of blend films from chitosan and hydroxypropyl guar gum." *Journal of applied polymer science*, Vol. 90, No. 7, pp 1991-1995.
- [32] Lim, H. J., Cho, E. C., Lee, J. A., & Kim, J. (2012) "A novel approach for the use of hyaluronic acid-based hydrogel nanoparticles as effective carriers for transdermal delivery systems." *Colloids* and Surfaces A: Physicochemical and Engineering Aspects, Vol. 402, pp 80-87.
- [33] Soppimath, K. S., Kulkarni, A. R., & Aminabhavi, T. M. (2001) "Chemically modified polyacrylamide-< i> g</i>-guar gum-based crosslinked anionic microgels as pH-sensitive drug delivery systems: preparation and characterization." *Journal of Controlled Release*, Vol. 75, No. 3, pp 331-345.
- [34] Huang, Y., Lu, J., & Xiao, C. (2007) "Thermal and mechanical properties of cationic guar gum/poly (acrylic acid) hydrogel membranes." *Polymer degradation and stability*, Vol. 92, No. 6, pp 1072-1081.
- [35] Wang, W. B., Huang, D. J., Kang, Y. R., & Wang, A. Q. (2013) "One-step< i> in situ</i> fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu< sup> 2+</sup> ion." *Colloids and Surfaces B: Biointerfaces*, Vol. 106, pp 51-59.
- [36] Liu, T. Y., & Lin, Y. L. (2010) "Novel pH-sensitive chitosan-based hydrogel for encapsulating poorly water-soluble drugs." *Acta biomaterialia*, Vol. 6, No. 4, pp 1423-1429.

- [37] Wang, W., Zheng, Y., & Wang, A. (2008) "Syntheses and properties of superabsorbent composites based on natural guar gum and attapulgite." *Polymers for Advanced Technologies*, Vol. 19, No. 12, pp 1852-1859.
- [38] Sandolo, C., Matricardi, P., Alhaique, F., & Coviello, T. (2009) "Effect of temperature and crosslinking density on rheology of chemical cross-linked guar gum at the gel point." *Food hydrocolloids*, Vol. 23, No. 1, pp 210-220.
- [39] Fujioka, R., Tanaka, Y., & Yoshimura, T. (2009) "Synthesis and properties of superabsorbent hydrogels based on guar gum and succinic anhydride." *Journal of applied polymer science*, Vol. 114, No. 1, pp 612-616.
- [40] Wang, W. B., Huang, D. J., Kang, Y. R., & Wang, A. Q. (2013) "One-step< i> in situ</i> fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu< sup> 2+</sup> ion." *Colloids and Surfaces B: Biointerfaces*, Vol. 106, pp 51-59.
- [41] Sandolo, C., Matricardi, P., Alhaique, F., & Coviello, T. (2009) "Effect of temperature and crosslinking density on rheology of chemical cross-linked guar gum at the gel point." *Food hydrocolloids*, Vol. 23, No. 1, pp 210-220.
- [42] Kawahara, J. I., Ohmori, T., Ohkubo, T., Hattori, S., & Kawamura, M. (1992) "The structure of glutaraldehyde in aqueous solution determined by ultraviolet absorption and light scattering." *Analytical biochemistry*, Vol. 201, No. 1, pp 94-98.
- [43] Whipple, E. B., & Ruta, M. (1974) "Structure of aqueous glutaraldehyde." *The Journal of Organic Chemistry*, Vol. 39, No. 12, pp 1666-1668.
- [44] Chen, Y., & Tan, H. M. (2006) "Crosslinked carboxymethylchitosan-g-poly (acrylic acid) copolymer as a novel superabsorbent polymer." *Carbohydrate research*, Vol. 341, No. 7, pp 887-896.

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