Synthesis of Poly(Acrylamide-Graft-Chitosan) Hydrogel: Optimization of The Grafting Parameters and Swelling Studies

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Abstract: Hydrogel polymers were prepared via graft polymerization of acrylamide (AAm) onto chitosan (CTS) backbone in the presence of methylene bisacrylamide (MBA) as cross-linker and ammonium persulfate (APS) as an initiator. Optimizing the crosslinking graft reaction of AAm onto CTS was studied by varying the concentration of CTS and MBA cross-linker and discussing the effect of these conditions on the gel fraction and the grafting parameters. The grafting parameters; grafting percentage (%GP), grafting efficiency (%GE), Add-on (%A) and homopolymer (%H) were studied as a function of the chitosan and the cross-linker concentrations. Also the swelling properties of the prepared hydrogel were examined. In this research, the simple second order kinetic model proposed by Schott has been carried out to describe the swelling mechanism. The effect of the grafting reaction on the thermal properties of the chitosan was also investigated by the thermal gravimetric analysis (TGA). The structure of the prepared hydrogel polymer was confirmed by FT-IR spectra. The porous structure of the hydrogel was observed by the Scanning Electron Microscope (SEM) and also the elemental composition of the prepared hydrogel was identified by using the energy dispersive X-ray (EDX).

Keywords: Acrylamide, Chitosan, Grafting, Hydrogel, Swelling

1. Introduction

Chitosan is derived from chitin by deacetylation using strong alkali. It is a safe polysaccharide and non-toxic. Chitin is a natural linear polysaccharide containing N-acetyl-D-glucosamine units and occupies second place on the earth next to cellulose. It is found in carapaces of Crustacea such as shells, crabs, lobsters, and shrimps. Usually, the Deacetylation of the chitin is incomplete and produces a copolymer containing D- glucosamine and N-acetyl-D-glucosamine units. The product from this deacetylation reaction is named chitosan [1, 2]. Chitosan has unique properties including biodegradability, nontoxicity and biocompatibility. It is sensitive to the pH of the medium as it readily dissolves at low pH while it is insoluble at high pH [3]. Although chitosan has commonly employed in various fields such as water treatment [4, 5, 6], drug release [7],

packaging films [8], and agriculture [9], many efforts are exerted to modify its structure by grafting and crosslinking to enhance specific properties such as the ability to absorb and retain large amount of fluid. This type of modification creates a material combining the properties of the natural material and the synthetic part. The kind of material which is a 3D crosslinked structure and capable of absorbing large amount of water is called hydrogel. The hydrogel is a water-swollen polymer which cannot dissolve in the medium of swelling as a result of their three-dimensional crosslinked network. The hydrogel is crosslinked through covalent chemical bonds and/or physical interactions/bonds such as hydrogen bonds, ionic and/or hydrophobic interactions. Recently, this material has gained considerable attention in the last years because of the need to exploit its unique properties in a wide range of applications such as drug delivery, metal and dye removal, agricultural uses, coal dewatering, and separation technology

[10-13]. The hydrogels are characterized by responding to the external stimulus. The chemical stimuli comprise ionic strength, pH, composition of the solvent and molecular species but the physical stimuli are magnetic/electrical field, pressure and temperature [14, 15, 16]. Various hydrogels have so far been developed using both of synthetic polymers such as polyacrylamide, polyacrylic acid and polyvinyl alcohol and natural polymers including hyaluronic acid, Cellulose, starch, chitosan, gelatin and alginate. Applications of the synthetic type are limited due to their high cost, dormant toxicity and serious environmental effects. Recently, the development of hydrogels based on natural polymers is more interesting due to their ecofriendly nature, biodegradability, low-cost production and abundant raw resources. Therefore, starch, cellulose, collagen, chitosan, β-Cyclodextrin and humic acid have been used to prepare hydrogels [17, 18, 19].

In this work, optimizing the crosslinking graft reaction of the acrylamide onto chitosan was studied by varying the concentration of chitosan and methylene bisacrylamide crosslinker and discussing the effect of these conditions on the gel fraction and the grafting parameters. Also the swelling properties of the obtained hydrogel were examined. The effect of the grafting reaction on the thermal properties of the chitosan was also investigated.

2. Experimental and Methods

2.1. Materials

Chitosan with deacetylation degree of 70-95% was purchased from Fluka. Acrylamide was obtained from sigma Aldrich Company Ltd (Germany). MBA and APS were obtained from Merck (Germany) and used as received. Analytical chemicals of NaOH pellets (99%) and HCl (36%) were purchased from Fluka and Merck, respectively. Distilled water was used for all experiments. The other chemical reagents were of analytical grade and used as received. The chemical structures of CTS, AAm, and MBA were shown in Figure 1.
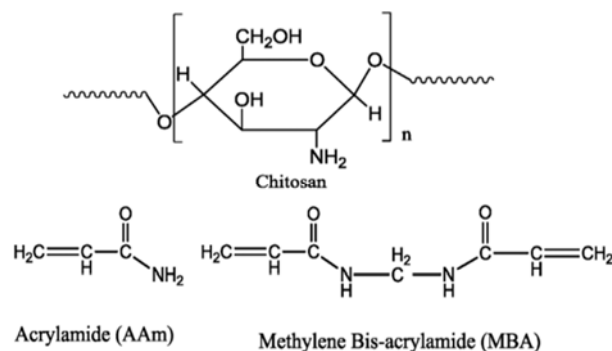

Figure 1. *The chemical structures of chitosan, acrylamide, and methylene bisacrylamide.*

2.2. Grafting of Acrylamide onto Chitosan

To optimize the grafting conditions, AAm was grafted on varied amounts of chitosan using varied amounts of MBA. For comparison purposes, P(AAm) gel was prepared by dissolving 3.551 (0.05 mole) of AAm in 50 ml distilled water, and to the resultant solution, 5×10^{-4} mole from APS (as an initiator) and MBA (as a cross linker) were added. Then the solution was purged with pure nitrogen and placed in a water bath adjusted at 70°C. The graft copolymer from AAm and CTS was prepared by the same way mentioned above there, but in this case 1%, 2%, 3%, and 4% of CTS solution (50 ml) was used instead of distilled water. The data of the feed compositions and the experiment conditions were summarized in Table 1. The produced gel in each experiment was washed first with 2% acetic acid solution then with water to remove ungrafted chitosan and to extract homopolymer, respectively. The pure graft copolymer was then dried and weighed.

Table 1. *The Feed compositions and the preparation conditions for AAm-g-CTS hydrogels.*

Sample code	CTS (g)	AAm (g)	MBA (g)	APS (g)	Acetic (1%) (ml)	Temperature (°C)	Time (h)
C0M1	0	3.55	0.077	0.114	50	70	2
C1M1	0.5	3.55	0.077	0.114	50	70	2
C2M1	1	3.55	0.077	0.114	50	70	2
C3M1	1.5	3.55	0.077	0.114	50	70	2
C4M1	2	3.55	0.077	0.114	50	70	2
C1M1.5	0.5	3.55	0.1155	0.114	50	70	2
C1M2	0.5	3.55	0.154	0.114	50	70	2

2.3. Gel Fraction

Simple method was employed to estimate the amount of the insoluble crosslinked part in the prepared gels (gel fraction). After leaving the samples immersed in distilled water for 48 h at 25°C then drying them until constant weight, the gel fraction was calculated according to the equation mentioned below:

$$\text{Gel fraction (\%GF)} = \frac{\text{Weight of the insoluble part}}{\text{Weight of the dried gel before swelling}} \times 100 \quad (1)$$

2.4. Estimation the Grafting Parameters

The grafting parameters; grafting percentage (%GP), grafting efficiency (%GE), Add-on (%A), and homopolymer (%H) were calculated by the following equations [20]:

$$\text{Grafting percentage (\%GP)} = \frac{\text{Grafted polymer}}{\text{Substrate}} \times 100 \quad (2)$$

$$\text{Grafting efficiency (\%GE)} = \frac{\text{Grafted part}}{\text{polymer formed}} \times 100 \quad (3)$$

$$\text{Add} - \text{on (\%A)} = \frac{\text{synthetic polymer}}{\text{Graft copolymer}} \times 100 \quad (4)$$

$$\text{Homopolymer (\%)} = \frac{\text{Homopolymer}}{\text{polymer formed}} \times 100 \quad (5)$$

2.5. Swelling Studies

To investigate the ability of the prepared gels to absorb water, a pre-weighed dried sample from each obtained gel was immersed in 50 ml distilled water at a temperature from 25°C to 50°C using tea bags. At various time intervals, the tea bag was taken out and wiped using filter paper to remove the water droplets on the surface, then the weight of the swollen sample was determined. The weight of the swollen sample was followed until the equilibrium is reached. This was repeated two times for each sample and the mean ±SD was taken. The equations mentioned below were used to calculate the swelling ratio (%SR), the swelling at equilibrium (%SE), and the equilibrium water content (EWC) [21, 22], respectively:

$$\%SR = \frac{\text{weight of swollen gel} - \text{weight of dry gel}}{\text{weight of dry gel}} \times 100 \quad (6)$$

$$\%SE = \frac{\text{weight of swollen gel at equilibrium} - \text{weight of dry gel}}{\text{weight of dry gel}} \times 100 \quad (7)$$

$$EWC = \frac{\text{Weight of swollen gel at equilibrium} - \text{weight of dry gel}}{\text{Weight of swollen gel at equilibrium}} \times 100 \quad (8)$$

2.6. Instrumentation

FT-IR was used to indicate the presence of the functional groups in the prepared gels and to be an evidence on the grafting reaction, and this was done on VERTEX 70 model, Bruker optics company (Germany) using potassium bromide disks under resolution 4 cm^{-1}. The thermal gravimetrical analysis (TGA) was used to investigate the thermal stability of the prepared gel and this was done under nitrogen atmosphere on a Shimadzu DTG-60/60H from room temperature to 600°C (20 °C / minute) using alumina powder as reference material. The scanning electron microscopy (SEM) was employed on the freeze dried samples for indicating the morphology of the prepared gels and this was done using SEM (Quanta 250 FEG with EDX Unit, FEI Company, Netherland) with an operating voltage 20 KV. Before carrying out the SEM examination, the freeze dried sample was fractured and gold-sputter coated to become electrically conductive.

3. Results and Discussion

3.1. Grafting Reactions

Graft polymerization reaction of acrylamide (AAm) has been carried out at different concentrations of chitosan and methylene bisacrylamide in distilled water using ammonium persulfate as an initiator. The grafting parameters; grafting percentage (%GP), grafting efficiency (%GE), Add-on (%A)

and homopolymer (%H) were evaluated as a function of the chitosan and the cross-linker concentrations (Table 2). The grafting reaction can be explained as follows: on heating the polymerization medium, the initiator molecules dissociate forming free radicals (NH$_4$OSO$_2$O$^{\cdot}$) which abstract hydrogen atom from NH$_2$ or OH groups on chitosan producing chitosan macroradicals. These macroradicals become free radical donors and the monomer molecules become acceptors. Chitosan macroradicals attach the monomer molecules resulting in chain initiation thereafter the radical sites transfer to the monomer molecules which become free radical donors to further neighboring molecules leading to the propagation. After propagation, the termination takes place by coupling the grafted chains together to give the graft polymer. The proposed mechanism of grafting of AAm onto chitosan was represented in *Figure* 2.
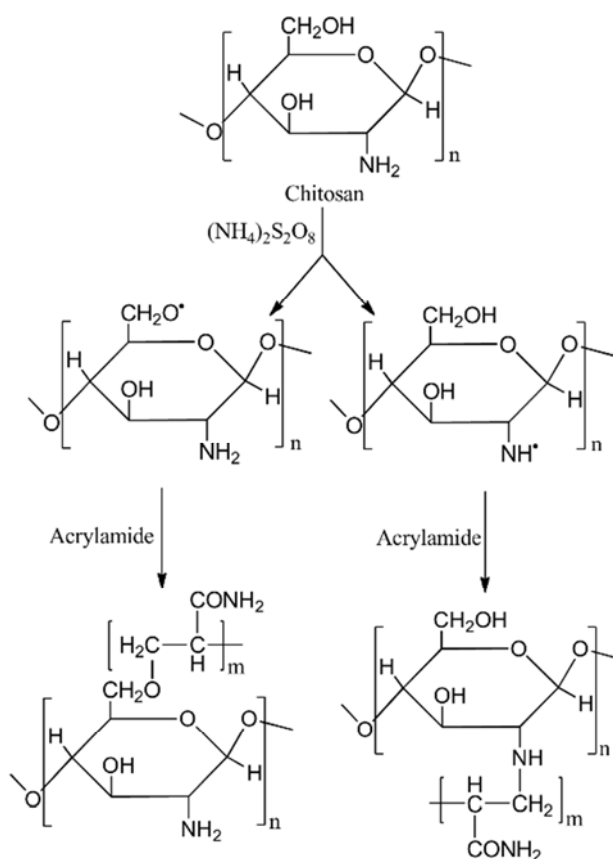

Figure 2. *The proposed grafting reaction of acrylamide on chitosan.*

Table 2. *Effect of chitosan and MBA on the gel fraction and grafting parameters.*

Sample	%GF	%GP	%GE	%A	%H
C0M1	76.8	-	-	-	23.2
C1M1	85.9	814.3	84.5	89.1	15.5
C2M1	80.3	304.8	73.9	75.3	26.1
C3M1	79.0	160.1	68.9	61.5	31.1
C4M1	78.3	69.2	62.6	40.9	37.4
C1M1.5	81.0	714.4	78.9	87.7	21.1
C1M2	80.2	722.4	78.1	87.8	21.9

3.1.1. Effect of Chitosan on the Gel Fraction

For comparison purpose, AAm was crosslinked by MBA in absence of chitosan and the gel fraction of the obtained hydrogel was 76.8%. As shown in Table 2 and Figure 3, this percent increased to be 85.9% after proceeding the grafting copolymerization in 1% chitosan solution instead of water. The increased gel percent may due to the generation of active sites on chitosan and act as macroradicals to attach more monomers forming the gel in presence of the crosslinker. This is accompanied by a decrease in the percentage of homopolymer formation from 23.2% for C0M1 to 15.5% for C1M1 sample. Beyond 1% chitosan, the gel fraction decreased. This may be due to the increase in the viscosity of the solutions after increasing the concentration of the chitosan. The increased viscosity makes the solutions heterogeneous resulting in less mobility of the macromolecules which may restrict it to recombine with each other. Another possible reason is the increase in the homopolymer formation.
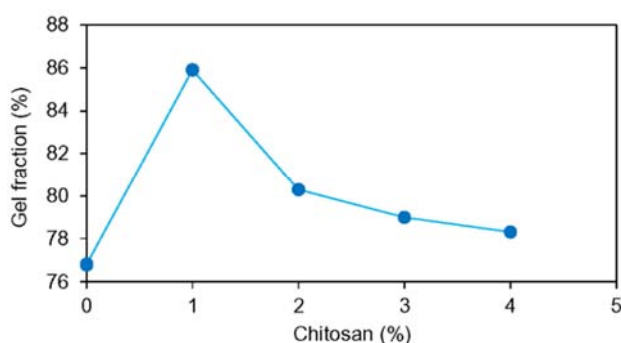

Figure 3. *Effect of chitosan concentration on the gel fraction.*

3.1.2. Effect of Chitosan on the Grafting Parameters

As shown from the Table 2 and Figure 4 the grafting parameters (grafting ratio, efficiency and add on) were decreased by increasing the concentration of chitosan and this may due to the increased viscosity of the reaction medium as the chitosan increases. The increased viscosity restricts the diffusion of the monomers in the reaction medium and this reduces the availability of the monomers at the active sites of the growing radical chains. An optimum grafting percentage (%G) value of 814.3 was obtained at 1% chitosan for acrylamide grafted chitosan.
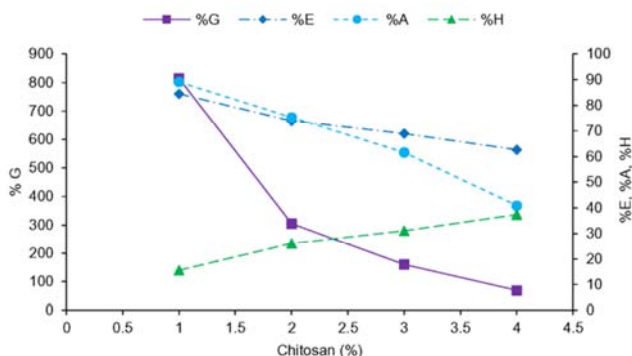

Figure 4. *Effect of chitosan concentration on the grafting parameters.*

3.1.3. Effect of MBA on the Gel Fraction

The experiments for studying the effect of MBA on the gel fraction showed that the sample C1M1 prepared using MBA (5×10^{-4} mole, 1% relative to moles of AAm) gave 85.9% gel fraction. As shown in Figure 5, increasing the MBA concentration from 1% to 2% led to a reduction in the gel fraction from 85.9% for C1M1 to 80.2% for C1M2 sample. This behavior may be attributed to the higher tendency of monomer to form homopolymer with increasing the MBA concentration. As shown in Table 2 percentage of homopolymer increased from 15.5% to 21.9% by increasing MBA from 1% to 2%, respectively. An optimum gel fraction value of 85.9% was achieved using 1% MBA (5×10^{-4} mole).
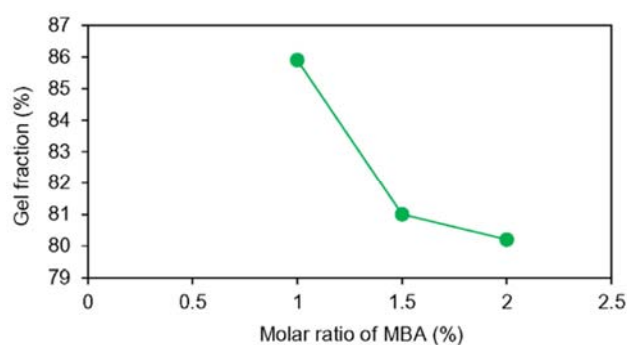

Figure 5. *Effect of MBA concentration on the gel fraction.*

3.1.4. Effect of MBA on the Grafting Parameters

The data in Table 2 showed that the grafting parameters (grafting ratio, efficiency and add on) were decreased by increasing the concentration of MBA from 1% to 2% (Figure 6). An optimum grafting percentage value of 814.3 was achieved using 1% MBA (5×10^{-4} mole).
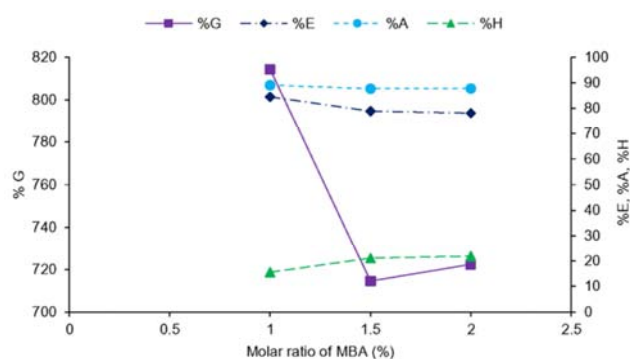

Figure 6. *Effect of MBA concentration on the grafting parameters.*

3.2. Swelling Studies

3.2.1. Effect of CTS on the Swelling

It was observed that from the tabulated data in Table 3, the equilibrium swelling degree (*%SE*) of AAm hydrogel (without chitosan; C0M1 sample) was 174 g/g polymer, and after grafting of AAm onto the chitosan the equilibrium swelling degree increased and became 260 g/g polymer as shown in Figure 6. This may be attributed to the availability of more hydrophilic groups (NH$_2$ and OH) on chitosan to which the water molecules are attached resulting in an

increase in the equilibrium swelling degree. However, increasing the chitosan concentration from 1% in C1M1 sample to 4% in C4M1 sample led to a decrease in the equilibrium swelling degree, as shown in Figure 7, and this observation may be explained as follows: The lowering of the equilibrium swelling degree from 260 g/g for C1M1 to

153 g/g for C4M1 may be due to the established crosslinking between the chitosan chains. At higher concentration from chitosan, excess chitosan free radicals are generated which combine again holding the neighbor chains together. This results in increasing the crosslinking which in turn reduces the equilibrium swelling degree.

Table 3. *The swelling values of the grafted AAm onto chitosan.*

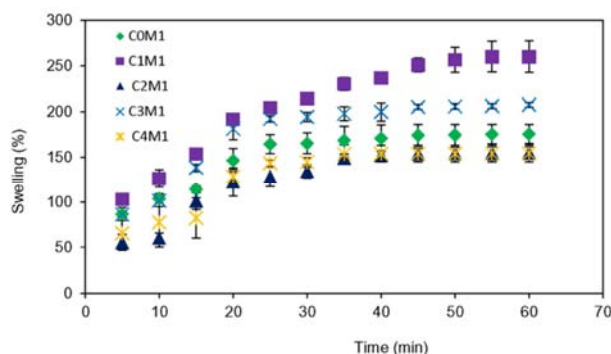|	C0M1	C1M1	C2M1	C3M1	C4M1	C1M1.5	C1M2
%SE	174±12	260±17	153±7	205±3	153±9	140±2	135±17
EWC	0.63±0.01	0.72±0.01	0.60±0.01	0.67±0.003	0.61±0.01	0.58±0.006	0.60±0.02

Figure 7. *Effect of chitosan concentration on the swelling.*

3.2.2. Effect of MBA on the Swelling

Also, the effect of MBA crosslinker on the swelling was studied and as shown from the data in Table 3 and plots of Figure 8 the swelling degree decreased from 260 g/g at 1% MBA in the sample C1M1 and become to be 135 g/g after duplication MBA concentration to 2% in the sample C1M2. This may due to increasing the crosslink density which limits the expansion of the hydrogel chains resulting in a reduction in the mount of water penetrated into the hydrogel. From the data mentioned in Table 3 the optimum swelling degree value of 260 g/g was achieved at 1% chitosan and 1% MBA (5×10^{-4} mole).

3.2.3. Swelling Kinetics

When a slightly crosslinked material is soaked in water, it does not dissolve but the water inters into the pre-existing pores in the crosslinked matrix and by the time the material swells. And this swelling pushes the material chains away from each other leading to increased separation between them causing overall segmental motion. The swelling mechanism is examined by several kinetic models. In our study, we used the simple second order kinetic model proposed by Schott [23, 24] as shown below:

$$t / S = A + Bt$$

Where S is the degree of swelling at time t, $B = 1/SE$ is the

inverse of maximum or equilibrium swelling and $A = 1/(k_s SE^2)$ is the reciprocal of the initial swelling rate (k_{is}) of the hydrogel, and k_s is the swelling rate constant. The above equation can be written as follows:

$$t/S = 1/(k_s\ SE^2) + 1/SE\ t \qquad (9)$$

Figure 8 presents the swelling kinetic graphs (t/S versus t) of the grafted AAm on the Chitosan hydrogels. The parameters SE, k_s, and k_{is} were calculated from the slope and intercept of lines of Figure 9 and the results are tabulated in Table 4. It is found that the values of these parameters are directly affected by the variation of chitosan and crosslinker concentrations. And by comparison, the theoretical values of SE are found to be similar to the swelling experiments.
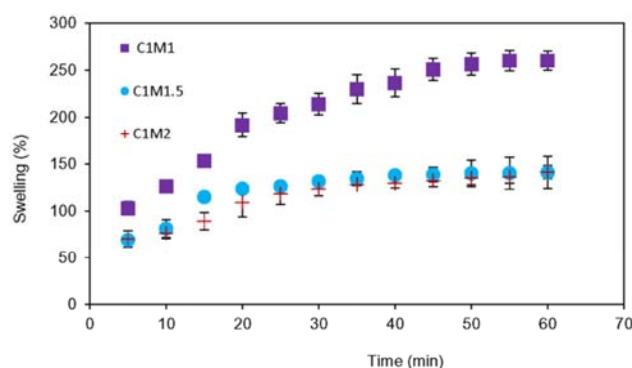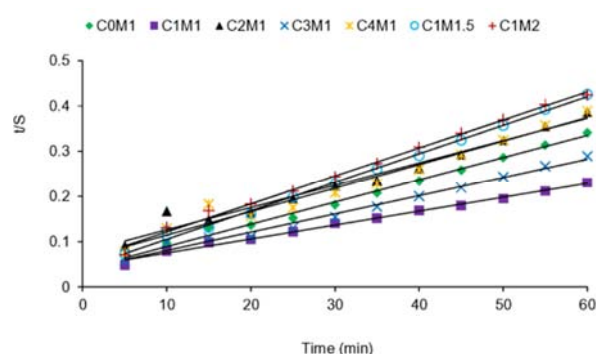

Figure 8. *Effect of MBA concentration on the swelling.*

Figure 9. *Swelling kinetic curves of grafted AAm onto chitosan.*

Table 4. *The swelling kinetic parameters of the grafted AAm onto chitosan.*

Swelling Kinetic Parameter	C0M1	C1M1	C2M1	C3M1	C4M1	C1M1.5	C1M2
Theoretical equilibrium swelling; (gwater/ggel. (SE)	203	325	202	248	192	158	161
Swelling rate constant; (ggel /gwater)/min. (Ks×10 -4)	6.11	2.15	3.19	4.08	4.35	9.51	6.47
Initial swelling rate; (gwater/ggel)/min. (Kis)	25.21	22.68	13.08	25	16.07	23.87	16.85

3.3. Characterization of the Prepared Hydrogels
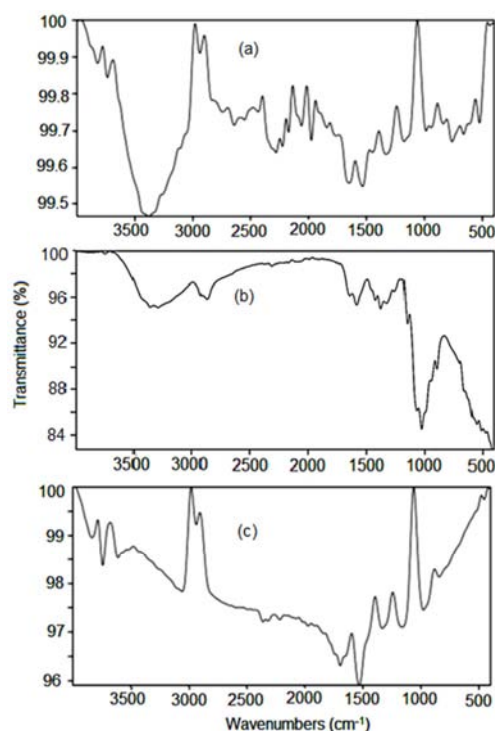
3.3.1. FT-IR Spectroscopy

Figure 10. *IR spectrum of (a) Polyacrylamide, (b) Chitosan, and (c) poly (acrylamide-graft-chitosan).*

Presence of the functional groups in the prepared hydrogel samples was confirmed by FT-IR spectra as shown in Figure 10. PAAm spectrum (Figure 10a) displays bands at 3378 cm^{-1} due to νN-H group and 1647 cm^{-1} ascribing to the νC=O group of the amide. The band at 2938 cm^{-1} is ascribed to aliphatic C-H stretching vibration. As it can be seen, the CTS spectrum (Figure 10b) shows mainly a broad absorption band around at 3289 cm^{-1} due to νO-H and νN-H. The bands at 1584, 1375, 1148 and 1025 cm^{-1} are assigned to δN-H of NH$_2$, -CH$_2$ bending, anti-symmetric stretching of the C–O–C bridge, and skeletal νC-O-C in anhydroglucose units, respectively [25]. IR spectrum of poly(acrylamide-graft-chitosan) hydrogel (Figure 10c) displays strong bands at 841, 977, 1160, and 1331 cm^{-1} which are characteristic bands of saccharide structure [26]. Appearance of a band at 1693 cm^{-1} which could be assigned to the stretching vibration of amide carbonyl group is a confirmation for the grafting reaction. Naturally the insolubility of AAm grafted chitosan in spite of containing a large number of amide groups is produced by the crosslinking [27]. The combined band at 3609 cm^{-1} could be assigned to O–H and N–H stretching in the grafted chitosan.

3.3.2. Thermal Analysis

TGA of the pure polyacrylamide hydrogel (Figure 11) shows a weight loss in three stages. The first stage occurs in the range of 170-240°C due to desorption of water on the surface and in the pores of the hydrogel. The second stage

ranges between 265 and 310°C (DTG peak at 282°C) and shows about 11.21% loss in the weight. This may be corresponding to the decomposition of the amide side groups in the form of ammonia and the crosslinker. The third stage of weight loss starts at 370°C and that continues to 445°C (DTG peak at 395°C) during which there was 33.86% of weight loss due to the degradation of the main backbone [28]. The TGA of the grafted product (Figure 11) supports the formation of the grafted chitosan-g-PAAm. It is observed in Figure 11 that the grafted polymer prepared using 14% chitosan relative to weight of acrylamide (C1M1 sample) begins to loss the adsorbed water at 182°C. The main decomposition stage of the natural part in the grafted product occurs in the temperature range from 206 °C to 219°C (DTG peak at 212°C) with a weight loss of 69.19% which is corresponding to random chain breaking and deacetylation of chitosan and decomposition of the amide groups from the grafted PAAm [29]. In the third stage, a weight loss of 7.9% occurs in the range of 371-433°C (DTG peak at 390°C) which is due to the decomposition of the main backbone of the grafted PAAm.
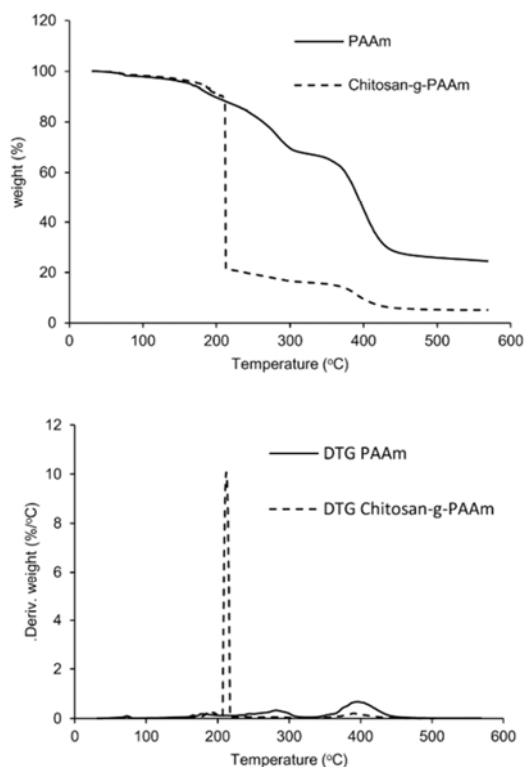

Figure 11. *TGA and DTG of polyacrylamide and chitosan-g-PAAm.*

3.3.3. Scanning Electron Microscope

The photographs taken by SEM at different magnifications of the swollen samples after freeze drying (Figure 12) verify the three dimensional porous crosslinked structures of the AAm grafted chitosan hydrogel. And then the presence of the crosslinks and pores makes the hydrogel insoluble and swell. Existence of these pores and spongy surface in the hydrogel strongly increases the swelling kinetics of the resulted

product. It is supposed that these pores are the regions of the water permeation and interaction sites of water molecules with hydrophilic groups of the hydrogel. The diameter of the pores were found to vary approximately from 6 to 12 μm.
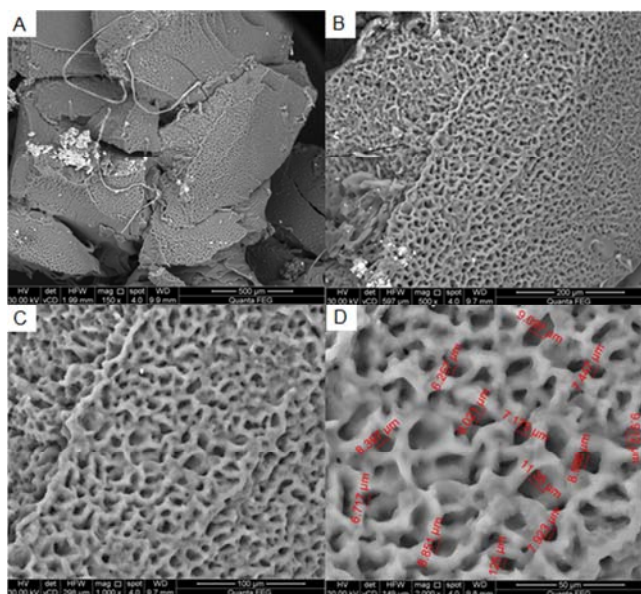

Figure 12. *SEM photographs of AAm grafted chitosan at different magnifications: (A) 150x, (B) 500x, (C) 1000x, and (D) 2000x.*

3.3.4. Energy Dispersive X-ray (EDX)

The energy dispersive X-ray (EDX) was used to identify the elemental composition of the hydrogels. Atoms of each element release X-rays with unique amounts of energy during the transfer process. The energies of the emitted X-rays can be used to identify the element. As shown in Figure 13 the EDX analysis of AAm grafted chitosan hydrogel revealed the presence (average wt%) of C (49.43), N (16.08), O (31.86) and Na (2.62).
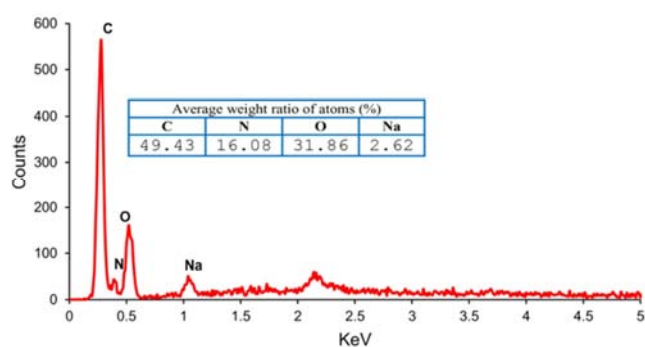

Figure 13. *EDX analysis for chemical composition of AAm grafted chitosan hydrogel.*

4. Conclusion

The hydrogels received much attention and are used in many fields because of their superior characters to traditional absorbents. In this work, Hydrogel polymers were prepared by crosslinking grafting the polyacrylamide onto chitosan. And the grafting parameters (grafting ratio, efficiency and add on) were found to decrease by increasing the concentration of chitosan. The obtained results also show that increasing of the concentration of MBA causes a decrease in the conversion of the acrylamide to the gel and in the grafting parameters. The grafting reaction enhanced the swelling of the grafted product which show swelling 260 g/g polymer and the maximum equilibrium swelling was achieved by using cross-linker ratio 1% relative to the acrylamide. The values of the swelling kinetic parameters are directly affected by the variation of chitosan and cross-linker concentrations. The theoretical values of SE are found to be similar to the swelling experiments. The prepared hydrogel polymer was confirmed by FT-IR spectra and thermal gravimetric analysis (TGA). The porous structure was observed by scanning Electron Microscope (SEM) and also the elemental composition of the prepared hydrogels were identified by using the energy dispersive X-ray (EDX). This study is a part of our current work which will be extended to use the prepared material for synthesis of bio-adsorbents system for application in wastewater treatment.

Acknowledgements

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