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Superabsorbent polyacrylamide grafted carboxymethyl cellulose pH sensitive hydrogel: I. Preparation and characterization

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ABSTRACT

Superabsorbent hydrogels were prepared by grafting copolymerization of cross-linked polyacrylamide chains onto carboxymethyl cellulose (CMC) via a free radical polymerization method. These graft copolymers hydrogel were characterized by infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. Hydrogels with different chemical composition were obtained through variation of grafting polymerization conditions such as CMC concentration, Acrylamide (AM) concentration, N,N´-methylene bis acrylamide concentration, Ammonium per Sulphate concentration, reaction time, and reaction temperature. The impact of hydrogels' composition on the water uptake capacity was monitored. Maximum water uptake, 158 g/g, was obtained with graft copolymer of 90% grafting percentage and 95% grafting efficiency compared to 37 g/g for the native polyacrylamide. Variation of CMC and AM concentration was found of determined effect. Direct impact of grafting percentage variation on the water uptake was observed. Sensitivity to pH of the swelling medium was recognized in both distilled and tap water. Sharp phase transition was recognized between pH 3.0 and 4.0 in swelling in tap water where this transition was broader in swelling in distilled water and recognized between pH 3.0 and 7.0. The hydrogel particle size was found also of determining effect where maximum swelling was observed with particles size ranged from 500 μm to 1000 μm. Maximum swelling was obtained at 40°C after 4 h swelling time at both tap and distilled water.

Keywords: Carboxymethyl cellulose; Graft copolymer; Polyacrylamide; pH sensitive hydrogel; Grafting; Swelling

1. Introduction

Highly swelling polymers, i.e. superabsorbent hydrogels, are hydrophilic three-dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight [1]. They are widely used in various applications such as hygiencs, foods, cosmetics, and in agriculture [2–4] which can be used as soil conditioners. Synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world [5–8]. Polymeric soil conditioners were known since the 1950s [9]. However, their wide commercial application failed even though the scientific basis for their use was quite well established. These polymers were developed to

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improve the physical properties of soil in view of: increasing their water-holding capacity, increasing water use efficiency, enhancing soil permeability, and infiltration rates. Several attempts have been made in the past to combine the best properties of both by grafting synthetic polymers onto natural polymers [10,11]. Recently, a new class of flocculating agents based on graft copolymers [12,13] of natural polysaccharides and synthetic polymers such as polyacrylamide (PAM) has been reported. The graft copolymers have also been found to be reasonably shear stable [14] because of the attachment of flexible synthetic polymers onto the rigid polysaccharide backbones.

Carboxymethyl cellulose (CMC) is an important industrial polymer with a wide range of applications. CMC is a derivative of cellulose and formed by its reaction with sodium hydroxide and chloroacetic acid. It has a number of sodium carboxymethyl groups (CH_2COONa), introduced into the cellulose molecule, which promote water solubility. Among all the polysaccharides, CMC is easily available and it is also very cheap. It has high shear stability. The structure of CMC is shown in Fig. 1. The use of CMC, an important modified polysaccharide, in gel formulations has not been extensively reported.

The present paper reports a study on the preparation and characterization of superabsorbent hydrogel by grafting cross-linked polyacrylamide chains onto CMC backbone by free radical polymerization for further enhancing the swelling degree of this natural polymer.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (CMC), (M wt. 90,000, DS = 0.7), was purchased from New Jersey (USA) in the form of sodium salt. Acrylamide (AM) (M wt. 71.08), purity 97%, was purchased from Sigma–Aldrich Chemie. N,N´-methylene bis-acrylamide (MBA) (M wt. 154.17, MP = 300) purchased from Sigma–Aldrich Chemie was used as cross-linking agent without any pre-treatment. Ammonium per sulfate (APS) (purity 99%, M wt. 228.2) was purchased from Sigma–Aldrich Chemicals Ltd (Germany). Other chemicals were of analytical grade and doubly distilled water was used throughout the experiments.

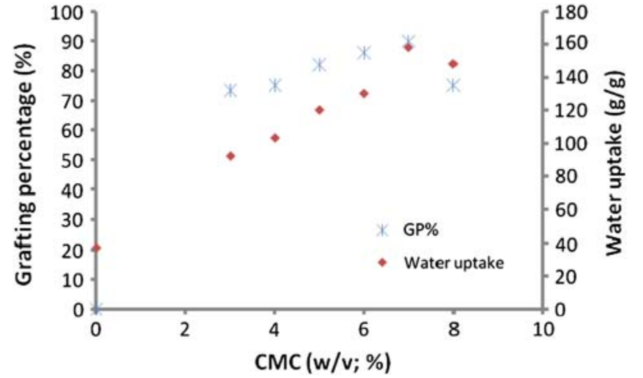


Fig. 1. Effect of variation CMC concentration on grafting percentage and water uptake (7% AM, 0.032% MBA, and 0.06% APS at 55˚C for 3 h).

2.2. Preparation of PAM-g-CMC hydrogel

The method of preparation of PAM-g-CMC hydrogel was carried out by a free radical polymerization method. In brief, into a beaker 500 ml the following components were dissolved in distilled water; CMC (7%), AM (7%), MBA (0.032%), and APS (0.06%) and the mixture was homogenized. The beaker was then kept in water bath at 55˚C for 3 h so that the contents changed into a gel-like mass. The gel so obtained was cut into small pieces and then washed by a suitable amount of hot distilled water at constant stirring rate (200 rpm) many times to remove the unreacted monomer and other chemicals. Acetone was used to squeeze the excess of water. The hydrogel so formed was dried overnight at 60˚C. The dry gel was crushed into nearly identical sized particles (500 μm–1 mm).

Different parameters have been monitored to evaluate grafting process namely: grafting percent (GP%), grafting efficiency (GE%), grafting conversion (GC%), and weight conversion (WC%) was calculated as follow:

$$GP\% = [(B - A)/A] \times 100 \quad (1)$$

$$GE\% = [(B - A)/(C + H)] \times 100 \quad (2)$$

$$WC\% = [(C + H)/D] \times 100 \quad (3)$$

$$GC\% = [(B - A)/D] \times 100 \quad (4)$$

where A is weight of CMC, B is weight of grafted polymer, C is weight of grafted polymer after extraction of homopolymer, H is weight of homopolymer, and D is weight of used monomer.

2.3. Preparation of polyacrylamide PAM (blank)

The same preparation method of PAM-g-CMC hydrogel was used in the preparation of cross-linked PAM hydrogel in absence of CMC under the same conditions.

It was then washed by a suitable amount of hot distilled water with stirring to remove the unreacted monomers and chemicals. Later on, acetone was used as a squeezer of water. The gel so formed was dried overnight at 60°C. The dry gel also was crushed and separated into different particle sizes using Sieve shakers.

The weight conversion (WC%) of monomers into polymeric hydrogel was determined from mass measurements [18] using the following expression:

$$\mathrm{WC\%} = \frac{\text{Total mass of polycrylamide formed}}{\text{Total mass of monomers in the feed mixture}} \times 100 \tag{5}$$

2.4. Water uptake (swelling) experiments

The progress of the water uptake (swelling) process was monitored gravimetrically as described by other workers [15]. In a typical swelling experiment, a pre-weighed piece of hydrogel (0.1 g) was immersed in an aqueous reservoir using distilled water (pH 7.2) and allowed to swell for a definite time period. At least three swelling measurements were performed for each sample and the mean values are reported. The swollen piece was taken out at predetermined time pressed in between two filter papers to remove excess water and weighed.

The water uptake and/or swelling degree percentage of hydrogel [16] can be determined as a function of time as following:

$$\text{Water uptake (g/g)} = m_t - m_0 \tag{6}$$

$$\text{Swelling degree (\%)} = [(m_t - m_0)/m_0] \times 100 \tag{7}$$

where m_t is the weight of the swollen hydrogel sample at time t and m_0 is the weight of the dry hydrogel sample.

The swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium. No buffer solutions were used and stock NaOH (pH 12.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

2.5. Characterization

The synthesized CMC-g-PAM, CMC, and PAM were characterized using Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan), thermogravimetric analyzer (Shimadzu TGA-50, Japan), and analytical scanning electron microscope (SEM) (Joel Jsm 6360LA, Japan).

3. Results and discussion

3.1. Grafting process

3.1.1. Effect of polymer (CMC) concentration

Fig. 1 shows the effect of variation CMC on the grafting percentage and the water uptake of the obtained graft copolymers. From the figure, it is clear that grafting percentage (GP) has influenced directly by variation the CMC concentration to have maximum value, 90%, with 7% CMC. Decrease of GP to 75% was obtained with graft copolymers prepared using 8% CMC. This behavior may be explained by increasing the sites of grafting which increases the possibility of grafting over the benefits of homopolymer formation. With CMC increment to 8%, the viscosity of the polymerization medium increases and diffusion of AM monomer molecules to reach the formed free radical sites on CMC backbone reduced. Accordingly, the grafting percentage reduced in favor of homopolymer formation.

This explanation is confirmed by the data obtained concerning the weight conversion, grafting conversion, and grafting efficiency percentages (Table 1) while the weight conversion remains constant, the grafting conversion and efficiency varied as grafting percentages. Our results are agreed with publishing data by other authors whom have the same finding [17,18]. On the other hand, the water uptake of the prepared hydrogel samples with different GPs was monitored. Similar behavior has been observed where water uptake was increased with GPs. Interesting finding has been observed from inspecting the figure regarding varied water uptake of hydrogel samples having equal GPs. Hydrogel samples with ≈75% GP prepared using 3%, 4%, and 8% CMC having water uptake 92 (g/g), 103 (g/g), and 148 (g/g), respectively. This behavior could be explained according to the number and length of grafted PAM chains in each hydrogel sample which directly affecting the network density.

Table 1
Effect of carboxymethyl cellulose (CMC) concentration on the weight conversion and grafting efficiency at constant conditions (7% AM, 0.032% MBA, and 0.06% APS at 55°C for 3 h)

CMC%	GE%	WC%	GC%
3	33.33	93.85	31.3
4	45.45	93.85	42.72
5	62.21	93.85	58.28
6	78.78	93.85	74.00
7	95.45	93.85	89.30
8	90.9	93.85	85.60

3.1.2. Effect of monomer (AM) concentration

Diffuse ability of monomers into the polymer matrix (CMC) has a great influence on the grafting percentage. Fig. 2 shows that increasing the monomer concentration (AM) clearly increased the grafting percentage. Grafting percentage was gone to highest value at 7% AM then tends to slightly decrease with further increase of AM concentration. These observations may be attributed to facilitate the diffuse ability of monomer towards the initiated sites on the cellulosic chains of carboxymethyl cellulose (CMC), upon increase the monomer concentration up to 7% which consequently increases the grafting yield. At monomer concentrations higher than 7%, the rate of radical formation on the monomer molecules becomes greater which affected the viscosity of the polymerization medium and also leads to increase the rate of termination process. This directly affected the degree of monomer conversion and diffusion through the polymer matrix, and hence the grafting percentage tends to decrease slightly. These observations are in agreement with similar observations reported by other authors [18–21]. This explanation is supported by data presented in Table 2 where grafting conversion clearly confirmed our expectations. The water uptake behavior was found similar to the GPs behavior. This is expected results since the cross-linked PAM grafted chains have a well-known hydrophilic characters responsible mainly about the water absorbance behavior.

Table 2
Effect of variation monomer (AM) concentration on the grafting conversion, grafting efficiency, and weight conversion at constant conditions (7% CMC, 0.032% MBA, and 0.06% APS at 55˚C for 3 h)

AM%	GC%	GE%	WC%
3	56.24	73.91	75.85
4	67.20	84.11	79.61
5	70.00	85.78	81.08
6	75.00	88.23	84.5
7	89.30	95.45	93.85
8	76.00	85.91	88.3

3.1.3. Effect of methylene bis-acrylamide (MBA) concentration

In the present study, methylene bis-acrylamide (MBA) acts as a cross-linker and also as a monomer. It was found that with increasing the concentration of MBA up to 0.032%, the grafting percent was increased up to maximum (90%) then tends to decrease slightly with further increase of MBA concentration as shown in Fig. 3. These results may be attributed to that with increasing MBA concentration up to 0.032%, MBA molecules acting in favor of cross-linking grafted PAM chains as "grafting from" and grafting PAM homopolymer chains to CMC backbone as "grafting to". Further increase of MBA leads to increase the cross-linking density of PAM-grafted chains in one hand and the cross-linking of PAM homopolymers chains on the other hand. Accordingly, the diffusion of left free AM monomer molecules will found a diffusion barrier which directly influences the grafting percentage.

This explanation is reinforced by the data presented in Table 3 where indicate that the WC% is almost constant. The grafting conversion percentage is identical to the obtained grafting percentage. The water uptake behavior was found identical to both of GC and GP percentages. Tighten of the network structure may be explained the water uptake behavior of hydrogel samples cross-linked with MBA concentration above 0.032% in addition to the low grafting percentage.

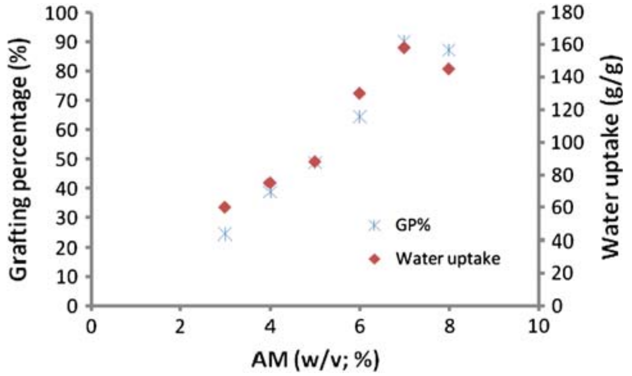


Fig. 2. Effect of variation AM concentration on grafting percentage and water uptake (7% CMC, 0.032% MBA, and 0.06% APS at 55˚C for 3 h).

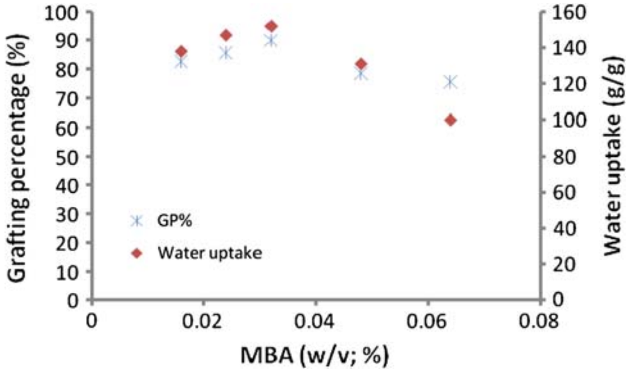


Fig. 3. Effect of variation MBA concentration on grafting percentage and water uptake (7% CMC, 7% AM, and 0.06% APS at 55˚C for 3 h).

Table 3
Effect of variation methylene bis-acrylamide (MBA) concentration on the grafting conversion, grafting efficiency and weight conversion at constant conditions (7% CMC, 7% AM, and 0.06% APS at 55°C for 3 h)

MBA%	GC%	GE%	WC%
0.016	82.00	87.69	92.64
0.024	85.60	91.32	93.53
0.032	89.30	95.45	93.85
0.048	78.12	84.09	92.79
0.064	75.33	80.91	92.72

Table 4
Effect of variation initiator (APS) concentration on the grafting conversion, grafting efficiency, and weight conversion at constant conditions (7% CMC, 7% AM, and 0.032% MBA at 55°C for 3 h)

APS%	GC%	GE%	WC%
0.03	74.6	81.8	90.7
0.06	90.0	95.45	93.85
0.12	82.85	88.54	93.33
0.24	80.0	87.09	91.43
0.48	77.1	84.37	91.01

3.1.4. *Effect of initiator (APS) concentration*

Fig. 4 shows the effect of variation APS concentration in the range (0.03–0.48%) on the obtained grafting percentage. It was clear that the maximum grafting percent was obtained at 0.06% APS and then slightly decreases with higher concentrations. These results may be attributed to increase number of free radicals and active sites on the polymer backbone with increasing initiator concentration up to 0.06% which leads to participate of higher number of monomer units in the grafting process and consequently increase the grafting percentage as shown by increasing the WC% (Table 4).

At higher concentrations beyond 0.06%, the grafting percentage decreases slightly and tends to leveling off mimics the behavior of WC%. Termination of higher number of formed free radicals presents an explanation of the obtained results which supported by the GC% results in Table 4. The water uptake of the obtained graft copolymer hydrogel samples obeyed the same behavior.

The obtained results are in agreements with previously published data by other authors even they used other types of initiation systems [18,22] such as gamma rays and cerric ammonium nitrate, although the variation in our case is not significant as that observed by other authors. This may be explained by the presence of cross-linker which acts as “coupling agent” to link the PAM homopolymer chains to the PAM-grafted chains on CMC. This will reduce the effect of free radicals terminations at high initiator concentration.

3.1.5. *Effect of grating temperature*

The effect of variation grafting’s temperature on the grafting percentages is illustrated in Fig. 5. It can be seen that there is an increment in the grafting percentage with increasing of temperature up to 55°C then tends to decrease with further temperature increment. The enhancement in grafting percentage of AM onto CMC chains from 67% to 90% upon raising the grafting polymerization temperature from 35°C to 55°C might be attributed to the following reasons [23,24].

Increasing temperature may be lead to:

(1) Increase the diffusion of AM from the solution phase to the swellable CMC phase.

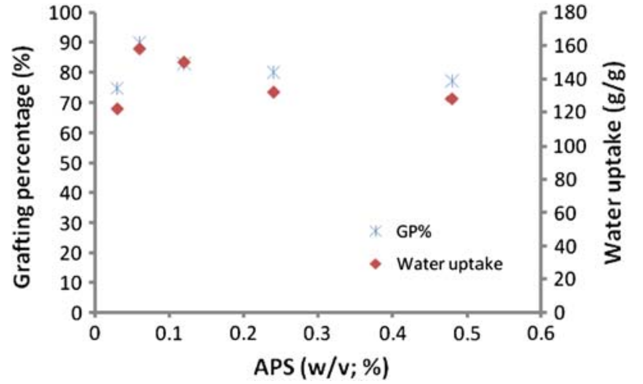


Fig. 4. Effect of variation APS concentration on grafting percentage and water uptake (7% CMC, 7% AM, and 0.032% MBA at 55°C for 3 h).

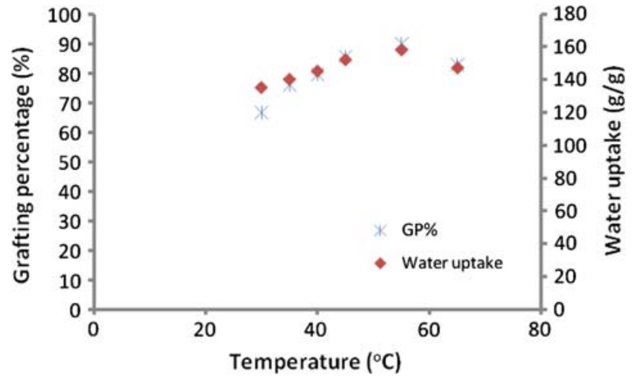


Fig. 5. Effect of variation polymerization temperature on grafting percentage and water uptake (7% CMC, 7% AM, 0.032% MBA, and 0.06% APS for 3 h).

(2) Increase the rate of thermal dissociation of APS, hence the rate of free radical formation on CMC backbone will increase.
(3) Increase the solubility of the monomer.
(4) Also increase formation and propagation of grafted chains.

The net effect of all such factors leads to high grafting with increasing the polymerization temperature. Higher temperatures beyond 55˚C may be lead to termination step occurring rapidly resulting in decrease the grafting percentage. This explanation is reinforced by the WC% data as shown in Table 5. The table also shows the variation of GC% and GE% with the same manner.

The water uptake behavior is identical with that of grafting percentage. This reflects the neglectable effect of variation polymerization temperature on the density of the formed graft copolymers network.

3.1.6. Effect of grafting time

The effect of variation grafting time on the studied grafting percentages is illustrated in Fig. 6. The results reveal that increasing the grafting time from 0.5 h to 2 h increase the grafting percentage to reach maximum value then tends to level off at 3 h and starts to decrease at 4 h. These observations could be explained in the light of increasing the number of formed free radicals in the grafting media with prolongation of polymerization time. Beyond 3 h of grafting time, higher number of formed free radicals accelerate the polymerization process as well as the viscosity of the grafting medium. Moreover, the diffusion rate of the monomer into the polymer chains will be reduced and hence the grafting percentage. This explanation was supported by WC% data which indicates the increase of WC% up to 2 h polymerization time then tends to level off at 3 h and starts to decrease after 4 h. The grafting conversion and grafting efficiency percentages follow the same behavior (Table 6). The water uptake trend obeyed the same attitude reflecting the effect of post-grafting time on the molecular weight and density of the formed network structure.

Table 5
Effect of variation grafting temperature on the grafting conversion, grafting efficiency, and weight conversion at constant conditions (7% CMC, 7% AM, 0.032% MBA, and 0.06% APS for 3 h)

Grafting Temperature(˚C)	GC%	GE%	WC%
30	66.43	91.3	72.52
35	72.68	91.88	79.09
40	79.60	92.52	85.6
45	85.50	95.087	89.73
55	89.30	95.45	93.85
65	73.80	89.92	82.48

3.2. Materials characterization

3.2.1. Infrared spectrophotometric analysis

The IR spectra of CMC, PAM, and PAM-g-CMC are shown in Fig. 7(a–c), respectively. From the IR spectra of CMC, it showed a broad absorption band at 3444 cm^{-1}, due to the stretching frequency of the –OH groups. The band at 2921 cm^{-1} was due to C–H stretching vibration. Appearance of a strong absorption band at 1618 cm^{-1} was due to the presence of COO^- groups. The bands around 1423 and 1326 cm^{-1} were assigned to CH_2 scissoring and –OH bending vibration, respectively. In the case of PAM, a broad absorption band at 3431 cm^{-1} was for the N–H stretching frequency of the NH_2 group. Two strong bands around 1689 and 1647 cm^{-1} were due to amide-

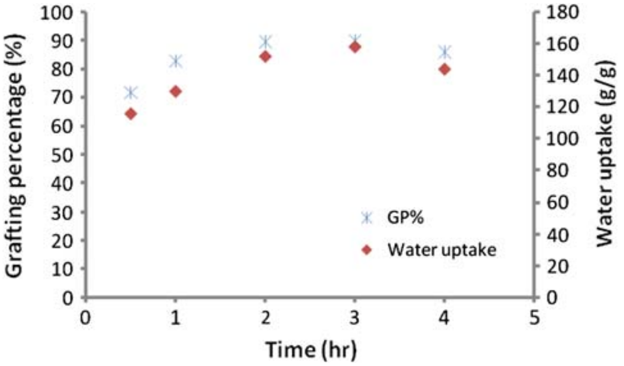


Fig. 6. Effect of variation polymerization time on grafting percentage and water uptake (7% CMC, 7% AM, 0.032% MBA, and 0.06% APS at 55˚C).

Table 6
Effect of variation grafting time on the grafting conversion, grafting efficiency, and weight conversion at constant conditions (7% CMC, 7% AM, 0.032% MBA, and 0.06% APS at 55˚C)

Grafting time (h)	GC%	GE%	WC%
0.5	71.28	88.07	81.05
1	82.31	93.54	88.16
2	87.43	94.34	93.00
3	90.00	95.45	93.85
4	86.00	94.06	91.01

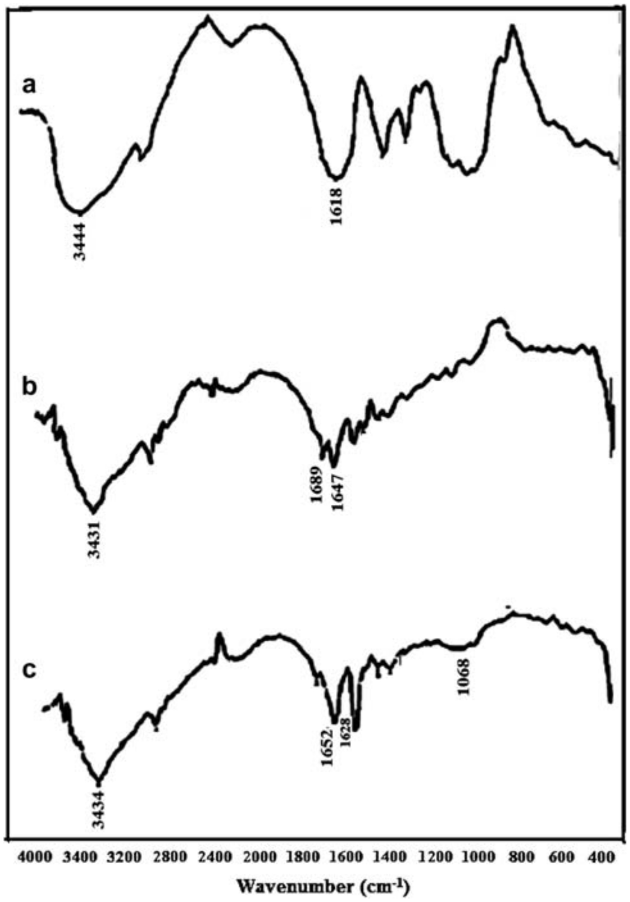


Fig. 7. FTIR of (a) CMC, (b) PAM, and (c) PAM-g-CMC.

I (C=O stretching) and amide-II (NH bending), respectively. The bands around 1400 and 2922 cm^{-1} were for the C–N and C–H stretching vibrations, respectively. Other bands at 1458 and 1323 cm^{-1} were attributed to CH_2 scissoring and CH_2 twisting. For IR spectrum of CMC-g-PAM, The presence of a broad absorption band at 3434 cm^{-1} was due to the overlap of –OH stretching band of CMC and –NH stretching band of PAM. A band at 1652 cm^{-1} was due to amide-I (C=O stretching) of the amide group of PAM and the band at 1618 cm^{-1}of CMC and amide-II band of PAM overlapped with each other and led to a broad band at 1628 cm^{-1}. The presence of a band at 1733 cm^{-1} was due to free acid groups. The bands around 1404 and 2922 cm^{-1} were for the C–N and C–H stretching vibrations, respectively. Other bands at 1458 and 1338 cm^{-1} were attributed to CH_2 scissoring and CH_2 twisting. Also, there was an important peak at 1068 cm^{-1} which assigned for the CH–O–CH_2 group resulting from grafting reaction between the hydroxyl group located in an hydroglucose C_2 position and the π-bond of PAM. The primary peaks existed in the PAM-g-CMC characteristic for the groups of AM, and the shift in the band corresponding to OH group, may suggest formation of ether (>CH–O–CH_2) during the grafting copolymerization [25]. Accordingly, it is apparent that FTIR presented a strong evidence of grafting of PAM branches onto the polysaccharide backbone; (since homopolymers were removed by solvent extraction).

3.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric curves of CMC, PAM, and PAM-g-CMC in a nitrogen atmosphere are displayed in Fig. 8. In the case of PAM, a continuous weight loss starting at the beginning of the heating was observed, and at least four thermal events. Above 240˚C the degradation of PAM is due to loss of ammonia with the formation of imide groups via cyclization [12]. Ammonia and water are the only volatile products below 340˚C in PAM [26]. Decomposition of the cyclic product was observed starting from 380˚C [12].

In general, the main decomposition of the polysaccharides starts above 200˚C. The first stage was attributed to desorption of moisture as hydrogen bound water to the polysaccharide structure. The second and third stages of decomposition took place at 241 and 307˚C, respectively, probably due to depolymerization with formation of water, CO, and CH_4 [27].

The pattern of copolymer thermal decomposition, exemplified by PAM-g- CMC, is different from those for the starting materials (CMC and PAM). The graft decomposition was observed in at least four stages.

The presence of PAM chains grafted onto CMC provoked a reduction in residue at 600˚C, from 37% (CMC) to 2.2–4.0% (grafts). This behavior has been

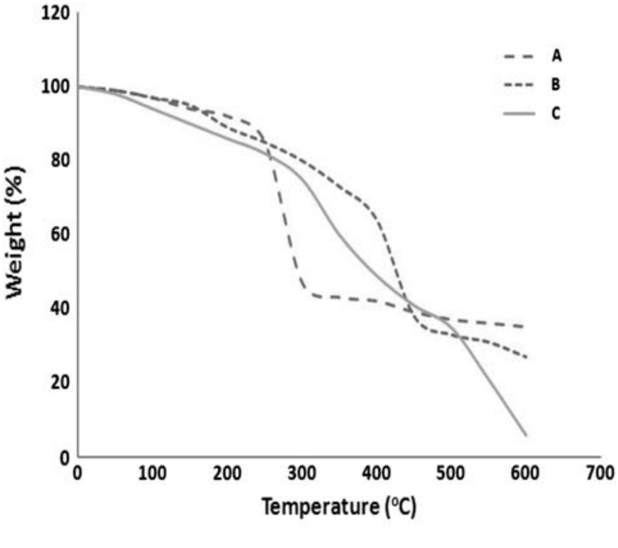


Fig. 8. TGA of (A) CMC, (B) PAM, and (C) PAM-g-CMC.

observed for sodium alginate [28] and polyacrylamide-grafted cashew gum [27]. The grafting of PAM chains onto the polysaccharide did not cause a significant change in the PAM thermal stability, but enhanced the CMC resistance to heat; perhaps due to the cross-linked nature of the homopolymer. This can also be proved by the T_{50} (the temperature at which the half weight loss occurs) which was 297, 417, and 391°C for CMC, PAM, and PAM-g-CMC, respectively.

3.2.3. Scanning Electron Microscope (SEM)

The scanning electron micrographs of CMC, PAM, and the graft copolymer (PAM-g-CMC) are shown in Fig. 9. It is clear that the morphological structure of both PAM and CMC differed from PAM-g-CMC. Surface morphology of CMC before grafting showed a granular structure, which has been changed to fibrillar form after grafting. It became more close to PAM morphology. Thus, the comparison of these figures reveals that grafting has taken place.

3.3. PAM-g-CMC hydrogels evaluation

Effect of variation different operational conditions such as swelling temperature and pH on the swelling process has been investigated. In addition, effect of hydrogels particle size on the swelling behavior has also been investigated.

3.3.1. Effect of the swelling medium temperature on the swelling degree of hydrogel

The effect of variation swelling medium's temperature on the swelling degree of PAM-g-CMC hydrogel was studied in the range of (30–60°C) as shown in Fig. 10. It is clear from results that the swelling degree was not much affected with increasing of swelling either in tap or in distilled water. On the other hand, acceleration of swelling equilibrium reach was noticed after 4 h at higher temperatures (≥40°C) compared to 5 h at temperature less than 40°C.

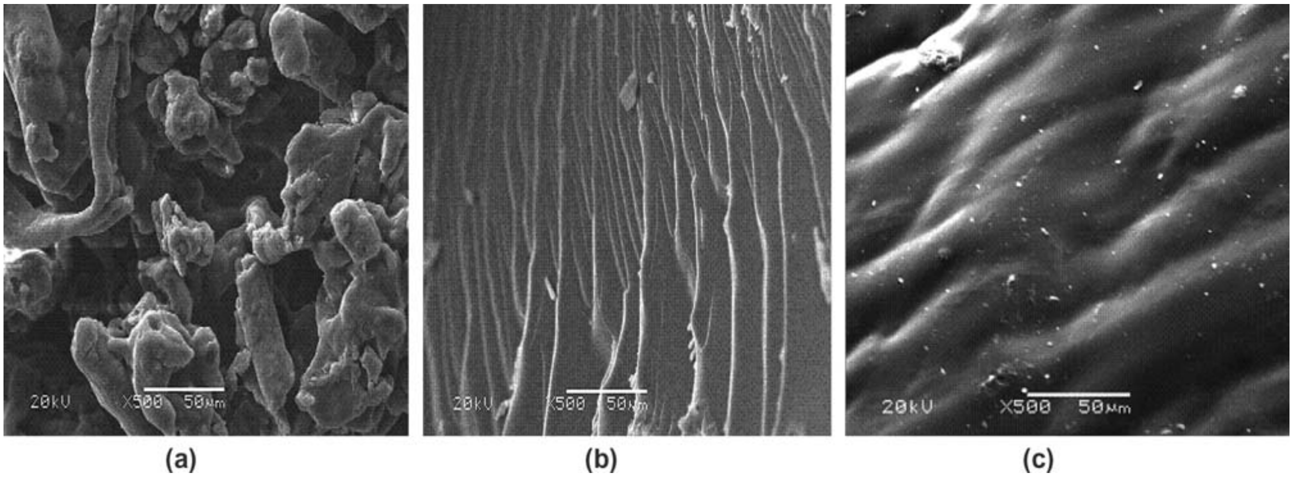
These results can be attributed to that with increasing temperature; the expansion and flexibility of gel network will increase and this leads to accelerate penetration of water molecules into gel network and shortened of swelling equilibrium time.

The insensitivity of the hydrogels to variation of swelling medium temperature may be referred to small particles size which increase the surface area subjected to water absorbance. This will lead eventually to reduce the mass transfer problem of water molecules into the three network structure of the hydrogel and consequently the swelling equilibrium time.

This behavior in fact could be consider as an advantage of our prepared hydrogel since there is no need for heating the swelling medium to obtain higher degree of swelling. Accordingly, the application of the prepared hydrogel in various applications will not be temperature dependent.

3.3.2. Effect of pH medium on the swelling degree of hydrogel

The effect of pH of the external solution on the swelling degree of hydrogel (CMC 7%, AM 7%, MBA 0.032%, and APS 0.06%) was studied in the range 1.0–11.0. It was observed in case of tap water that the swelling degree was increased sharply from pH 3 to pH 4, and beyond pH 4 it remains nearly constant as shown in Fig. 11(a), while it was observed that the



(a) (b) (c)

Fig. 9. SEM of (a) CMC, (b) PAM and (c) CMC-g-PAM.

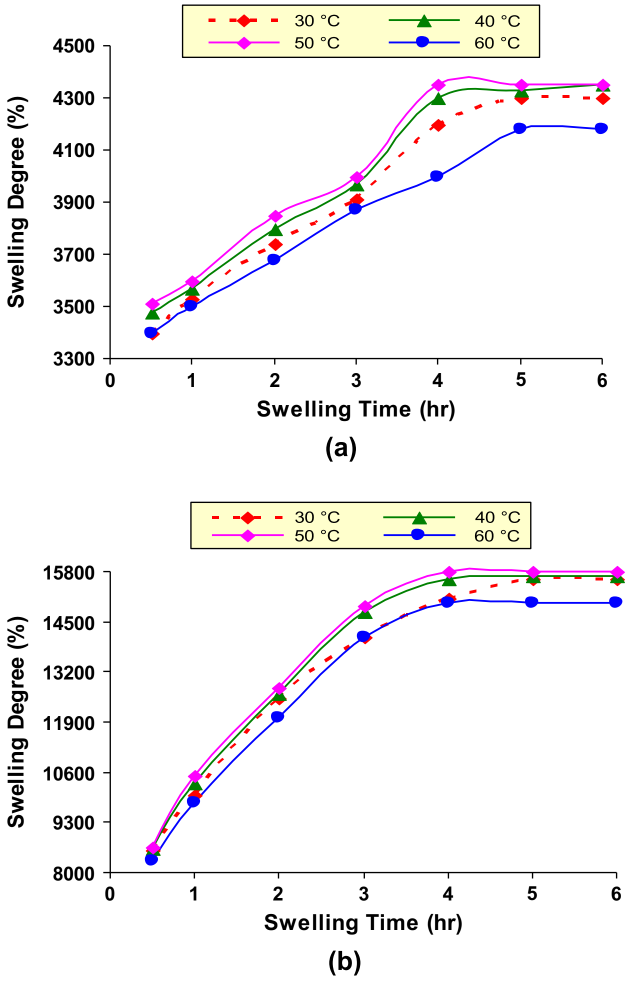


Fig. 10. Effect of variation in temperature of the swelling medium on the swelling degree (SD%) of hydrogel, (CMC) 7%, (AM) 7%, (MBA) 0.032%, and (APS) 0.06% at 55℃ for 3 h; (a) tap water and (b) distilled water.

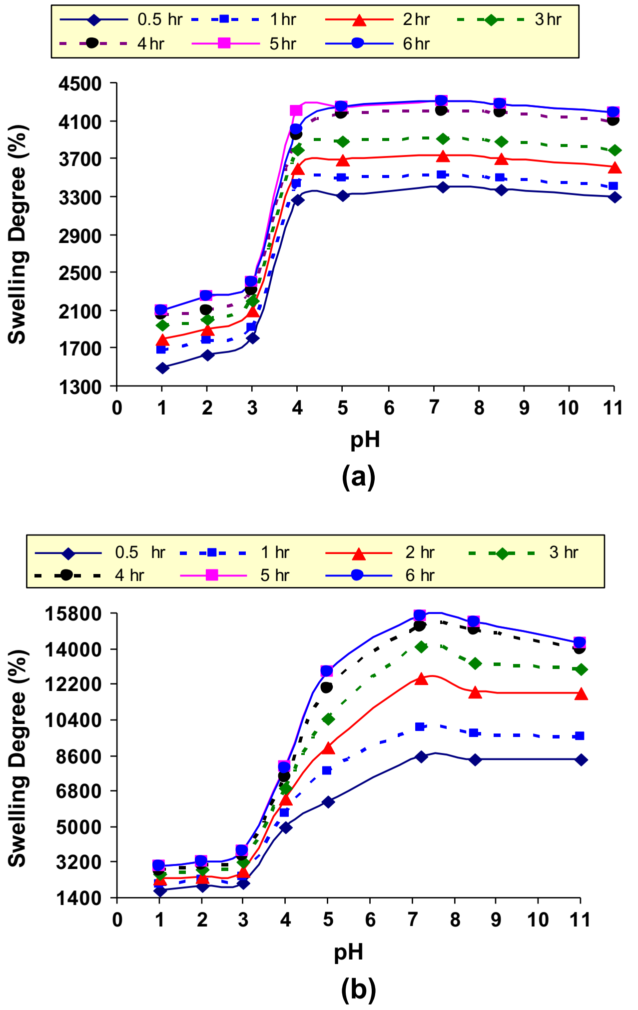


Fig. 11. Effect of variation in pH of the swelling medium on the swelling degree (SD%) of hydrogel, (CMC) 7%, (AM) 7%, (MBA) 0.032%, and (APS) 0.06% at 55℃ for 3 h; (a) tap water and (b) distilled water.

swelling degree in case of distilled water was increased gradually where it reached to maximum at pH 7.2 then tends to slightly decrease as shown in Fig. 11(b). The same behavior has been observed by other workers where they studied the swelling of carboxymethylcellulose–poly(sodium acrylate-co-acrylamide) hydrogel in distilled water under varied range of pH (1.0–12.0) [29]. They found that maximum swelling (107 g/g) was obtained at pH 8. They explained the obtained results according to the following. Under acidic pHs (≥ 3), most of the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and consequently the swelling decreased. However, some sort of attractive interactions (H–O and H–N hydrogen bonding) lead to decreased absorbencies. On further increase in the pH (3–8) the swelling capacity surprisingly improved. This can be attributed to the fact that with increasing pH of the external solution, the carboxylic acid groups of the hydrogel are converted to carboxylate anions. This obviously results in an expansion of the network chains causing to an increase in absorbency amount. Similar swelling pH dependencies have been reported in the case of other hydrogel systems [30–33]. The same explanations presented by those authors can be used in our case.

The different swelling behavior in tap water may be attributed to the presence of large concentrations of different salts, where the total dissolved salts (TDS) in all experiments equal to 458 ppm and the conductivity 914 µs, but in the case of distilled water not higher than 1.8 ppm and conductivity 2.05.

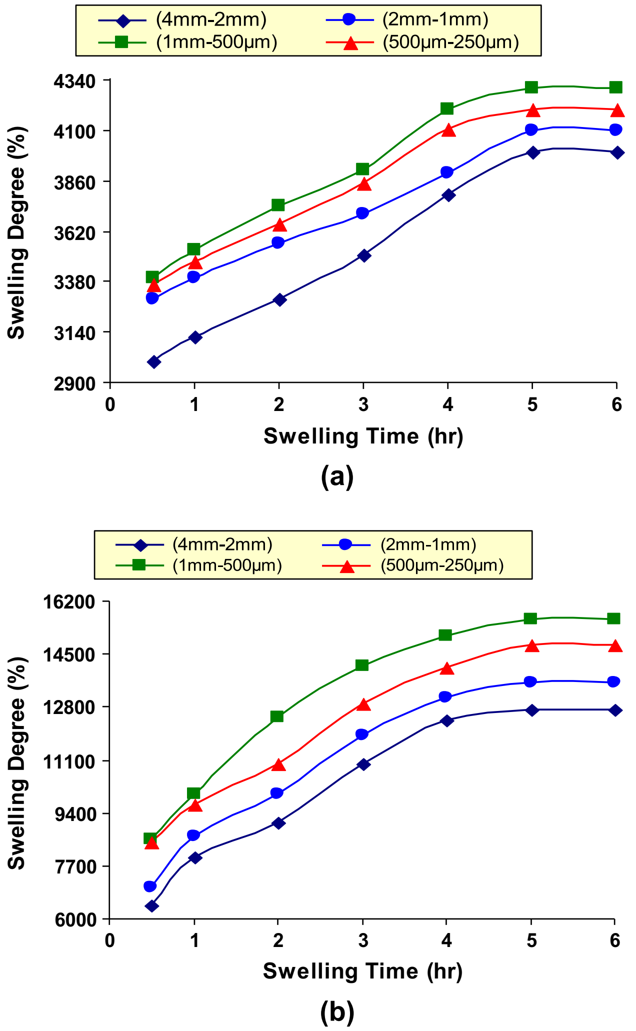


Fig. 12. Effect of variation in particle size on the swelling degree (SD%) of hydrogel, (CMC) 7%, (AM) 7%, (MBA) 0.032%, and (APS) 0.06% at 55˚C for 3 h; (a) tap water and (b) distilled water.

3.3.3. Effect of particle size on the swelling degree of hydrogel

In practical applications, a higher swelling rate is required as well as a higher swelling capacity. It is well known that the swelling kinetics for the absorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area, and composition of polymer.

The influences of these parameters on the swelling capacity have been investigated by various workers [34,35]. For example, the dependency of water absorbing capacity of SAPs on particle size was investigated by Omidian et al. [36]. Results indicated that as the particle size became smaller, the rate of absorption increased. This may be attributed to an increase in surface area with decreasing particle size of samples. The same findings were also observed by Mohammad Sadeghi and Hossein Hosseinzadeh during their studies of swelling behavior of carboxymethylcellulose poly(sodium acrylate-co-acrylamide) hydrogel [29].

The effect of variation in particle size, in the range of 4 mm–250 µm, on the swelling degree of (CMC-g-PAM) hydrogel is observed as shown in Fig. 12. It was clear from results that the swelling degree increased gradually with lower particle size. These results are in agreement with those obtained by other authors [29,36].

4. Conclusion

From this study, it was found that the grafting of polysaccharides such as CMC by synthetic polymers as PAM will increase of the water uptake capacity of this natural polymer to have superabsorbent hydrogel. The water uptake capacity of grafted hydrogel was found depend on the concentrations of the feed compositions of the hydrogel, and the best preparation conditions is [CMC] 7%, [AM] 7%, [MBA] 0.032%, and [APS] 0.06% at 55˚C for 3 h where we got a highest percentage of grafting (90%), highest grafting efficiency (95%), and highest water uptake capacity (158 g/g). Maximum water uptake reaches 158 g/g compared to 37 g/g for the native PAM. Characterizations by FT-IR, TGA, and SEM provide further proof of grafting process on the backbone of CMC.

Sensitivity to pH of the swelling medium was recognized in both distilled and tap water, where sharp phase transition was recognized between pH 3.0 and 4.0 in swelling in tap water, where this transition was less sensitive in swelling in distilled water and recognized between pH 3.0 and 7.0. The swelling degree at distilled water was found much higher than that at tap water as a result of salt sensitivity of the grafted hydrogel. The hydrogel particle size was found also of determining effect where maximum swelling was observed with particles size ranged from 500 µm to 1000 µm. Smaller particles size has less swelling capacity. Fast equilibrium was established at elevated temperature where maximum swelling was obtained at 40˚C after 4 h swelling time at both tap and distilled water. The sensitivity of the hydrogel towards temperature of the medium was much higher at tap water than at distilled water.

The prepared cross-linked PAM-g-CMC hydrogel shows good thermal stability, high water absorbency, high pH, and salt sensitivity which recommended our preparation for biotechnological and agricultural applications.

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