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Characterization of Super-Absorbent Material Based on Carboxymethylcellulose Sodium Salt Prepared by Electron Beam Irradiation

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Crosslinked CMC-N/PAAm hydrogel were prepared using electron beam irradiation. The factors affecting the degree of crosslinking and swelling behavior of the prepared copolymer were determined. As the irradiation dose and/or PAAm concentration increase, the gel content increases. Preparation of super-porous hydrogel was attained by the addition of ammonium carbonate as a gas-blowing agent during the irradiation process. The surface morphology and pore structure of such a prepared hydrogel were examined using scanning electron microscopy. The ability of the prepared hydrogel to absorb and retain large amount of water and as simulating urine was measured. The results suggested the possible use of CMC-Na/PAAm hydrogels in the personal care product industry.

Keywords CMC-Na, polyacrylamide, super-absorbent, swelling, radiation

Introduction

Super-absorbent hydrogels are crosslinked hydrophilic polymers that differ from conventional hydrogels in being capable of absorbing and retaining water and other aqueous mixtures hundreds of times beyond their own weight, without being dissolved. Because of their versatile and unique properties, super-absorbent hydrogels have vast potential applications, including soil/water stabilization layers in farming and civil engineering structures (1), soil conditioners, controlled release of fertilizers (2, 3), fiber and metallic cable sealing (4), in water technologies (5), thickening agents for cosmetics (6), in drug delivery systems (7) and many other fields. One of the most dynamic fields in which the super-absorbent hydrogels play the principle role is in the manufacture of personal care products such as feminine hygiene products, adult incontinence products and disposable diapers (8).

Today, all the disposable diapers in the markets enclose fast absorbent materials merely formed from acrylate-based polymers that do not readily decompose, and thus, represent a source of solid wastes rapidly filling up the landfills. In addition, the

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area of human skin in direct contact with the partially neutralized cross-linked synthetic polymer in the diaper may suffer from irritation to the extent where the epidermis may peel off (9). Therefore, the utilization of natural-based polymers became a necessity.

Cellulosic materials are capable of absorbing large amounts of water. However, they cannot retain this absorbed water and other aqueous mixtures. This is because they lack a three-dimension structure. Radiation processing had been demonstrated on a large commercial scale, to be a very effective tool for the improvement of various polymers properties. The reactions of crosslinking, degradation and grafting on polymers, initiated by radiation, had found many useful applications (10, 11). CMC-Na was previously believed to undergo degradation upon radiation treatment (12). The primary event, upon the CMC-Na exposure to high-energy radiation in the dry form, includes the formation of ions resulting from the scission of the main polymer backbone bonds C−C, C−O or C−H. These ions are rapidly converted into free radicals, which are responsible for the subsequent polymer degradation (13).

Recently, some attempts were made to crosslink cellulosic materials by radiation in the presence of a definite amount of water (14–17). However, such crosslinks were so weak that they were easily broken down under the influence of moderate temperature.

In this respect, trials were made to crosslink CMC-Na and CMC-Na/PAAm blends using electron beam irradiation. The probability for such crosslinked hydrogels to have potential use in the manufacturing of disposable infant diapers was discussed.

Materials and Methods

Materials

Commercial polyacrylamide (PAAm) powder MW 5,000,000-6,000,000 and high viscosity CMC-Na; degree of substitution not less than 0.4, were used as received.

Preparation of Hydrogels

Appropriate weights of dry CMC-Na and PAAm were mixed with water at different concentrations, put in polyethylene bags (the thickness of the bags filled with samples was 3 mm) and irradiated at different doses using an electron accelerator of electron energy: 1.45 MeV, electron beam current: 4 mA, scanner width: 90 cm and conveyor speed at $20\,kGy:\ 3.6\,m \cdot min^{-1}$. After irradiation, the prepared polymers were dehydrated by the aid of an ethanol-water mixture (80, 90, and 99%), dried at 37°C for 24 h, and stored in a vacuum oven at 40°C for 12 h before use.

Gel Determination for Hydrogels

In order to determine the insoluble parts of the hydrogels, the prepared samples were extracted with water for 24 hrs at 50°C. The gelled part, was taken out and washed with water to remove the soluble fraction, then dried and weighed.

The gel percent in the hydrogel was determined from the following equation:

$$\mathrm{Gel}(\%) = (W_E/Wg) \times 100$$

where, W_E and Wg represent the weights of the dry hydrogel after and before extraction, respectively.

Swelling Measurement

The dried and ground polymers of known weights were put in stainless steel net bags and immersed in distilled water or simulated urine solutions (18) at 25°C. The bags were removed from the solution at regular intervals of time, blotted quickly with absorbent paper and then weighed. The experiment was repeated three times for each sample and the average weight of swelled polymer was taken. The following equation was used to determine the swelling ratio of the hydrogels.

$$\text{Swelling ratio (g/g)} = (\text{Ws} - \text{Wg})/\text{Wg}$$

where, Ws and Wg represent the weights of wet and dry gel, respectively.

SEM Examination

The samples were immersed in distilled water for 20 min, freeze dried, and examined with the use of a JEOL-JSM-5400 (Japan) scanning electron microscope (SEM) after gold deposition in vacuum for 3 min.

The total uncertainty for all experiments ranged from 3–5%.

Biodegradation Study

Samples of known weights were put in stainless steel bags and buried in clay soil. The bags were removed from soil, cleaned up and weighed at regular intervals of time for detecting the % loss in weight.

Results and Discussion

Figure 1 shows the effect of different irradiation doses and polymer concentrations on the gel content of CMC-Na after extraction at 35°C. The applied irradiation dose has a significant effect on the CMC-Na gel content, prepared at a concentration of 50%. As the irradiation dose increases the gel content increases to reach its maximum at 20 kGy. Thereafter, any increase in the irradiation dose leads to an insignificant change in CMC-Na gel content.

Also, it is clear that there is a relationship between the degree of crosslinking and the CMC-Na concentration. The increase in the concentration is accompanied by a significant increase in the gel content; the degree of crosslinking of 50% CMC-Na concentration is higher than that of 40% CMC-Na, while there is no gel obtained when 30% CMC-Na was irradiated under the same conditions.

The results assumed that; the crosslinking reaction occurred due to the presence of hydroxyl radicals from water as a result of the effect of radiation. These radicals subsequently abstract hydrogen atoms from the anhydro-glucopyranose rings, creating macro radicals on the polymeric backbone. Free radicals formed in the CMC-Na may then couple directly or rearrange to more stable radicals. Such coupling reaction requires a finite lifetime for the radical species and sufficient mobility for their diffusion, which depends on the water percent or the concentration of the CMC-Na polymer.

At extremely low concentration, the crosslinking process minimized as the radicals produced have great mobility and thus, the rate of the coupling reaction could be insufficient to cause gelation.

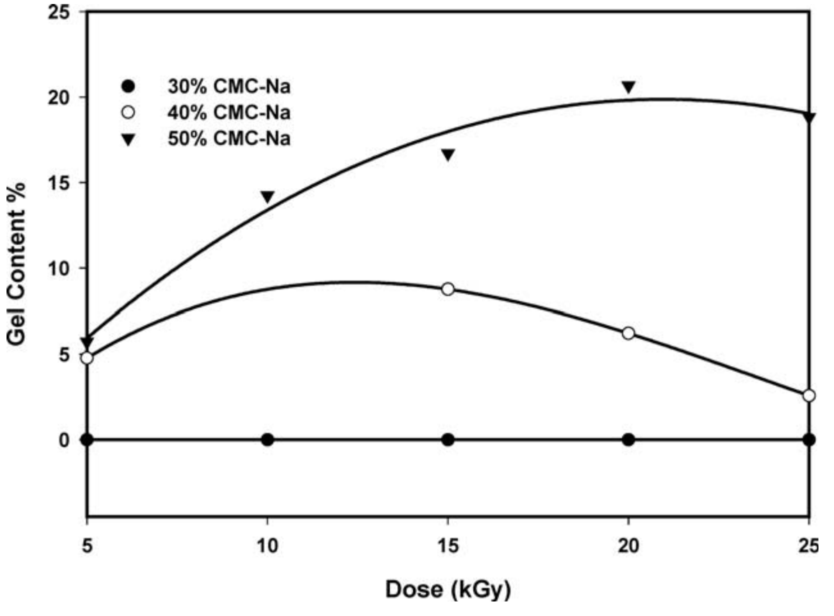

Figure 1. The gel content of crosslinked CMC-Na prepared at different compositions and extracted at 35°C.

On the other hand, the noted crosslinking reaction competes actively with the facile chain degradation reaction during irradiation process. If irradiation is continued to higher doses, the material may be degraded and soluble once again. Therefore, to obtain crosslinked CMC-Na, a definite amount of water and suitable irradiation dose should be considered.

The maximum gel content obtained for crosslinked CMC-Na at room temperature was less than 25%. However, complete dissolution of the irradiated samples extracted at 50°C, in distilled water, occurred. This shows the very weak reversible crosslinks may be formed by the action of radiation. Therefore, trials were made to improve the gel content of the CMC-Na by mixing it with a definite amount of PAAm. Figures 2 and 3 show the effect of different copolymer compositions on the gel content of the obtained CMC-Na/PAAm copolymers, extracted at room temperature and 50°C, respectively. The increase in the PAAm content in the blend composition leads to an increase in the degree of crosslinking. The maximum gel content was obtained at approximately 15 kGy; any further increase in irradiation dose leads to insignificant change in copolymer gel content. The gel content extracted at room temperature is higher than that extracted at 50°C.

Under the effect of irradiation, the degraded chains of CMC-Na react directly with PAAm, which is a crosslinkable type of polymer, to form graft copolymer of crosslinked structure. Thus, the ability of CMC-Na, to form a stable network structure, was enhanced.

At high irradiation doses, >15 kGy, the translocatory motion of the chains will be limited, due to the increase of crosslinking content. Hence, the frequency of collision of free macro radicals is reduced. Consequently, the crosslinking reaction is minimized and no significant increase in gelation is observed.

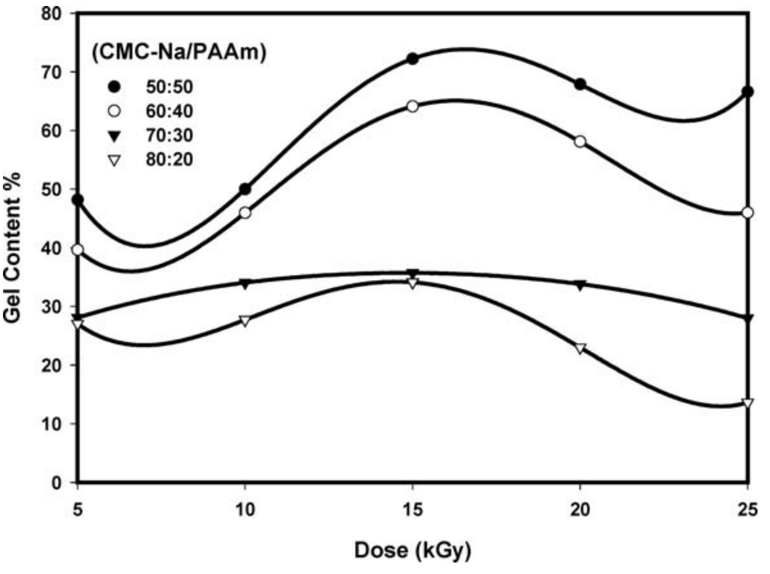

Figure 2. The gel content of crosslinked CMC-Na/PAAm as a function of irradiation dose. The samples prepared at different compositions and extracted at 35°C.

Swelling Character of the Prepared Hydrogel

The basic feature of super-absorbent hydrogel is in its ability to absorb and hold large amounts of liquid hundreds of times greater than its own weight without dissolving in it. There is a relationship between the degree of swelling and the nature of both the polymer and the liquid. A representative swelling curve of the CMC-Na hydrogel in

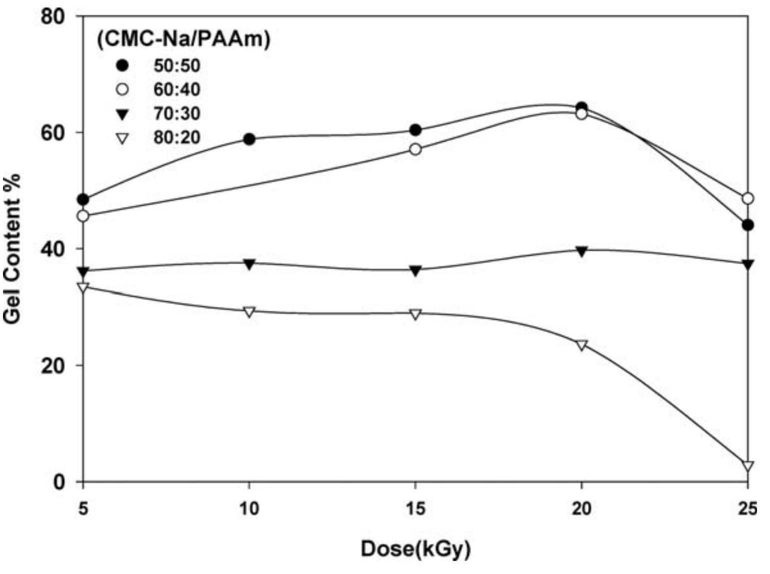

Figure 3. The gel content of crosslinked CMC-Na/PAAm as a function of irradiation dose. The samples prepared at different compositions and extracted at 50°C.

distilled water is shown in Figure 4, where there is a mutual increase in the amount of absorbed water with the increase in the CMC-Na concentration.

The results assumed that the swelling can be attributed to the nature of CMC-Na; being hydrophilic in character due to the presence of hydroxyl groups on the chain backbone in addition to the carboxy-methylate groups ($-CH_2COONa$). The later are readily ionized in water creating an electrostatic repulsion forces between the polymer chains, which results in increasing the swelling property.

On the other hand, 30% CMC-Na, having the lowest gel content, was expected to give the highest swelling degree. But, in fact, this was not the case as it gave the lowest value compared to the other hydrogels of different CMC-Na concentrations. This may be due to the weak reversible network structure which readily dissolves in distilled water and thus minimizes its water holding capacity.

Another contributing factor that controls the degree of swelling is the irradiation dose, which affects the degree of crosslinking. From Figure 5, it can be seen that the increase in the applied dose is accompanied by an increase in the degree of swelling due to the network formation till certain value (30 kGy), after which any further increase in the irradiation dose leads to a decrease in the swelling ratio. This behavior may be attributed to the degradation of the CMC-Na under the influence of radiation.

PAAm was added in different amounts, in order to increase the gel content of the CMC-Na hydrogel under low irradiation doses. Thus, better insoluble hydrogel with

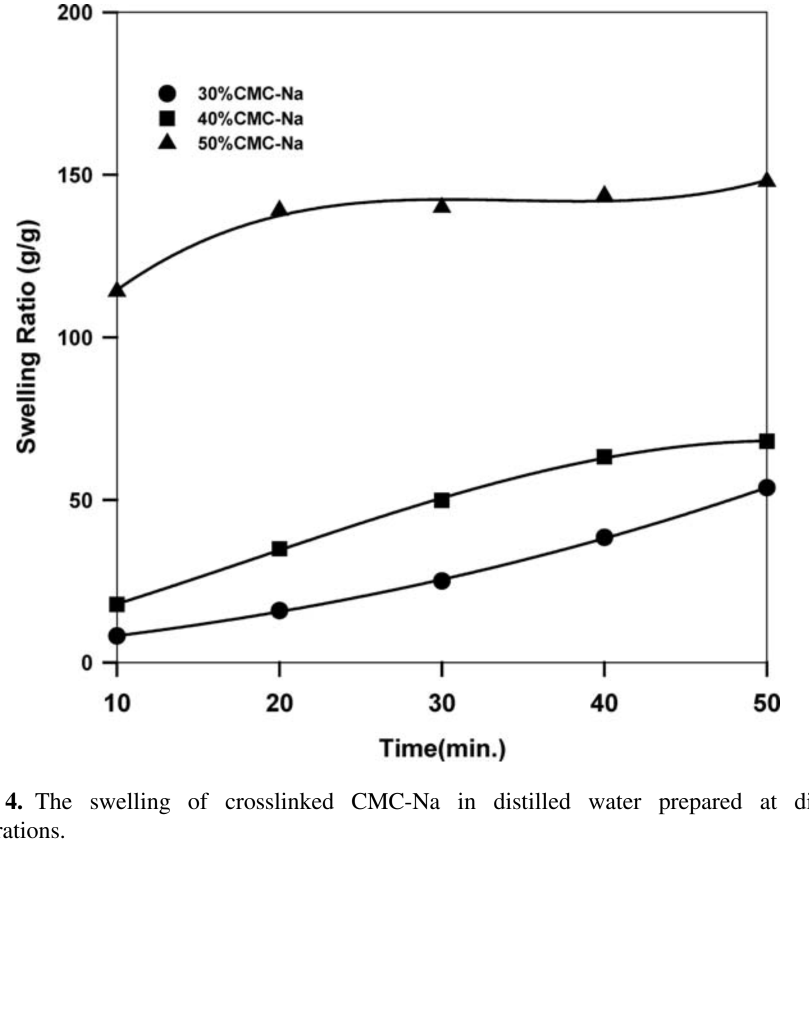

Figure 4. The swelling of crosslinked CMC-Na in distilled water prepared at different concentrations.

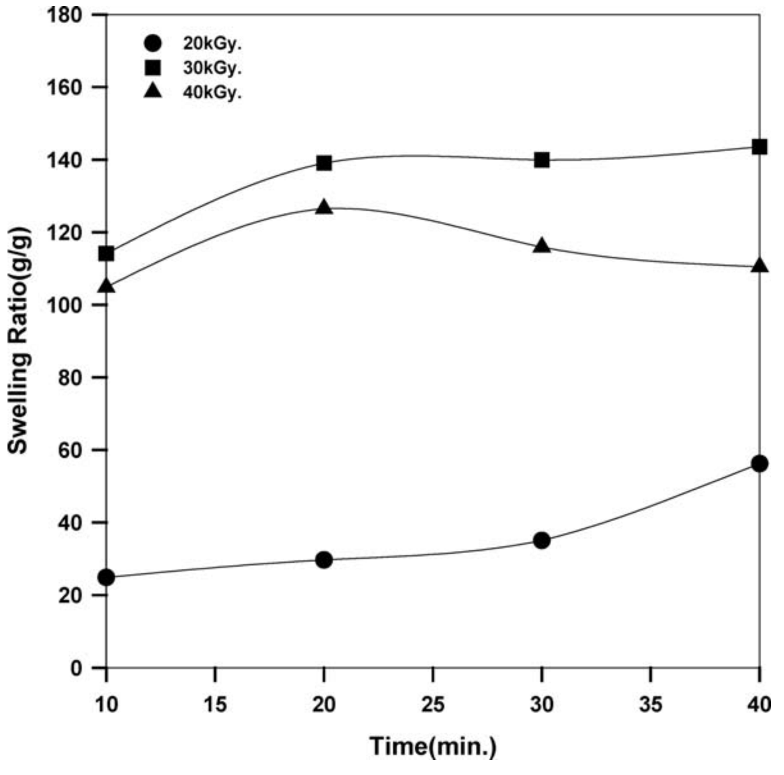

Figure 5. The swelling ratio of crosslinking CMC-Na in distilled water. The samples prepared at different irradiation doses.

higher water holding capacity is obtained. Figure 6 shows the swelling of CMC-Na/PAAm copolymers of different compositions, prepared at a fixed irradiation dose. In general, the swelling of CMC-Na/PAAm copolymer is higher than that of PAAm. There is a clear relation between the content of PAAm in the blend and the swelling degree. The increase in the PAAm content is correlated with a mutual increase in the water absorbing capacity. The CMC-Na network structure may be improved by adding PAAm.

Super-porous Hydrogels

While slow swelling of dried hydrogel has been beneficial for many applications, there are situations where fast swelling of dried hydrogels in the order of minutes rather then hours is desirable. The most common method for reducing swelling time of the hydrogel was by decreasing the diffusion path length i.e., reducing the dimensions of the hydrogel. However, this approach has an obvious disadvantage since it limits the hydrogel to certain types of applications. More advanced method to overcome this obstacle, is the incorporation of porogens or gas blowing agent such as ammonium carbonate during the preparation of such hydrogels (19, 20).

The effect of the added ammonium carbonate, as a gas-blowing agent, during the copolymerization of CMC-Na/PAAm blends on their swelling behavior is demonstrated in Figure 7. It is clear that the presence of the blowing agent not only reduces the time for

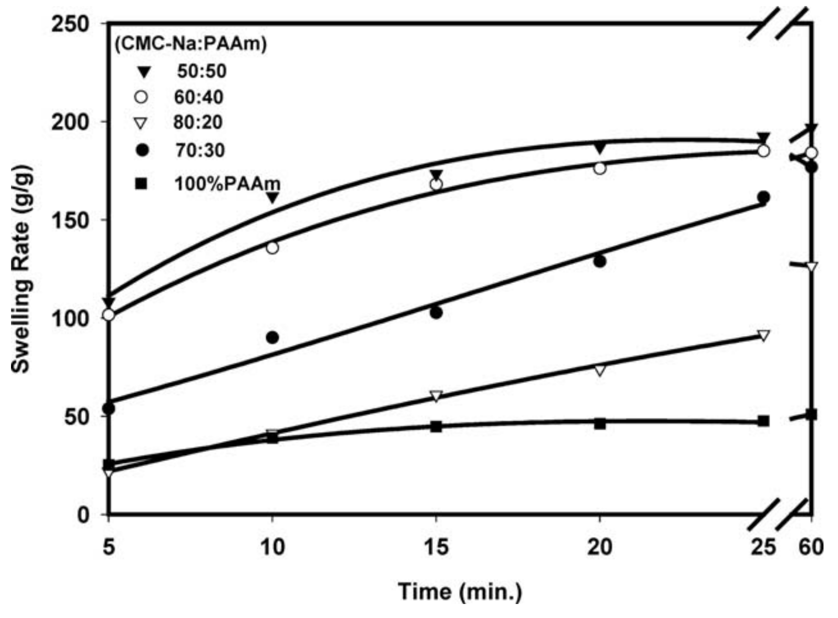

Figure 6. The swelling of CMC-Na/PAAm hydrogels in distilled water. The hydrogels prepared at different compositions and irradiated at 15 kGy.

equilibrium swelling, but also enhances the swelling ratio in comparison with that prepared in the absence of a blowing agent.

During the irradiation process, ammonium carbonate decomposed to CO_2 and NH_3, which are responsible for the formation of interconnected pores inside the hydrogel

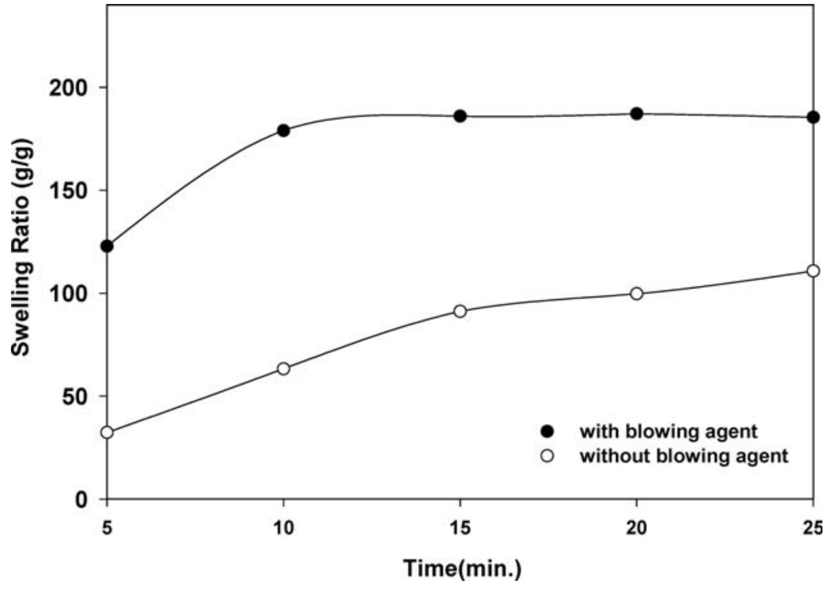

Figure 7. The swelling ratio in distilled water of super-absorbent CMC-Na/PAAm hydrogels prepared in the presence or absence of ammonium bicarbonate.

(21). Fast swelling of the prepared hydrogel may be attributed to the absorption of liquids by capillary forces rather than by simple diffusion, via the opened channels formed by the inter-connected pores.

To preserve the inter-connected capillary structure of the hydrogel, the samples were dehydrated using ethyl alcohol before air-drying. This prevents the pore walls from adhering to each other during the drying process (22).

Scanning Electron Microscope

The pore structure at the surface of the prepared hydrogels was thought to be important for their fast swelling property. Thus, freeze-dried CMC-Na/PAAm super-absorbent hydrogels, prepared at different irradiation doses were examined by SEM as shown in Figure 8(a–c). It is clear that the crosslinking density formed during the irradiation process seriously affects the pore structure of the prepared super-absorbent hydrogel. The gel of low crosslinking density forms a relatively wide pore structure Figure 8(a) but, those of high crosslinking density randomly aggregated and exhibited a granular structure of narrow pore size Figure 8(b,c). As the irradiation dose increases, the crosslinking density of the gel increases and their pore size decreases.

Temperature Effect on Swelling of the Copolymer

For investigating the effect of temperature on the hydrogel-swelling ratio, the water uptake measurement was performed at 15°C, 25°C, and 37°C as shown in Figure 9. It is clear that by the increase in the temperature, there is a significant increase in the swelling ratio. When the temperature increases from 15°C to 37°C, the rate of water diffusion enhances and the mobility of the polymer chains also increases, as a consequence, the water sorption capacity increases.

Potential Application of Prepared Hydrogel

The swelling of the prepared super-porous hydrogel was investigated for its possible use in personal care articles, particularly diapers. Thus, its degree of swelling was measured in simulating urine solution, and compared with commercial super-porous hydrogels based on acrylate polymers, as shown in Figure 10. It is clear that there is a slight difference between the swelling of the prepared CMC-Na/PAAm hydrogel and the commercialized one in the simulated urine solution. The prepared crosslinked copolymers possess high and fast swelling properties in simulated urine media. An acceptable swelling capacity for super-absorbent is approximately 20–40 g of urine per gram of hydrogel (8, 23). Therefore, the swelling ratios of CMC-Na/PAAm gels in urine are acceptable for diaper application.

On the other hand, a remarkable decrease in the swelling ratio measured in simulated urine solution, compared with that measured in distilled water, was observed (Figure 11). Increasing the ionic concentration of the simulated urine reduces the mobile ion concentration difference between the polymer gel and the external solution and thereby, reduces the gel swelling (24).

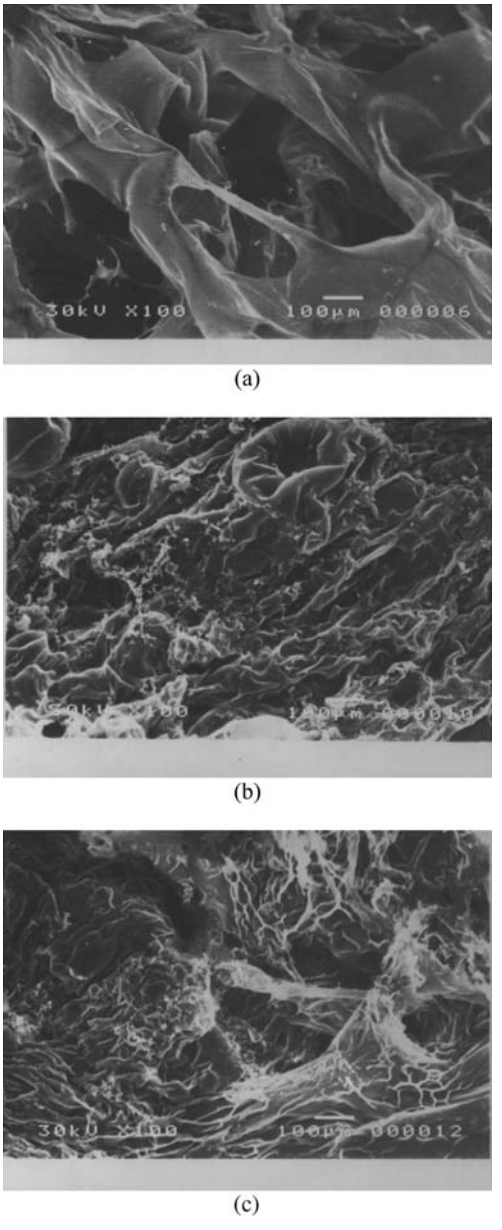

Figure 8. SEM for (CMC-Na/PAAm) hydrogel prepared at different compositions. (a) (80/20), (b) (60/40), and (c) (50/50).

Biodegradability

The prepared hydrogels were examined for their biodegradability by burring a known weight of the samples in soil at 35°C for different time intervals. Despite the three-dimensional network structures of the hydrogel, significant degradation in the buried samples took place after 60 days as shown in Table 1. Also, it is observed that the

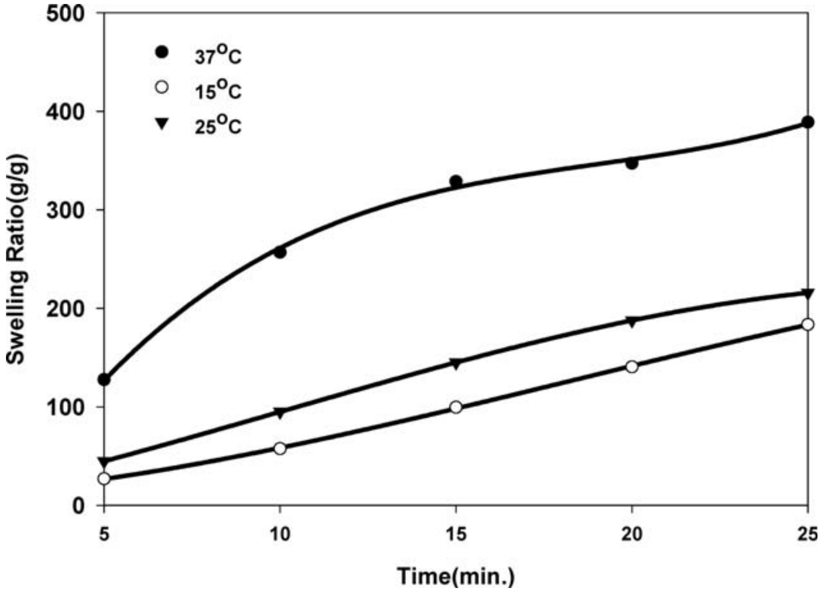

Figure 9. The swelling ratio of crosslinked CMC-Na/PAAm in distilled water at different temperatures.

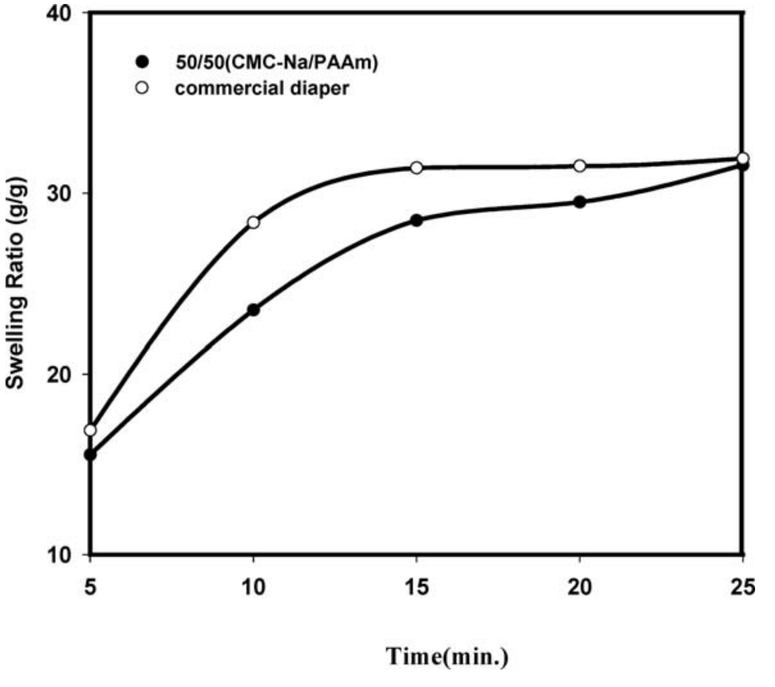

Figure 10. The swelling ratio of (●) CMC-Na/PAAm super-absorbent hydrogel, (○) commercial diaper; in simulated urine solution.

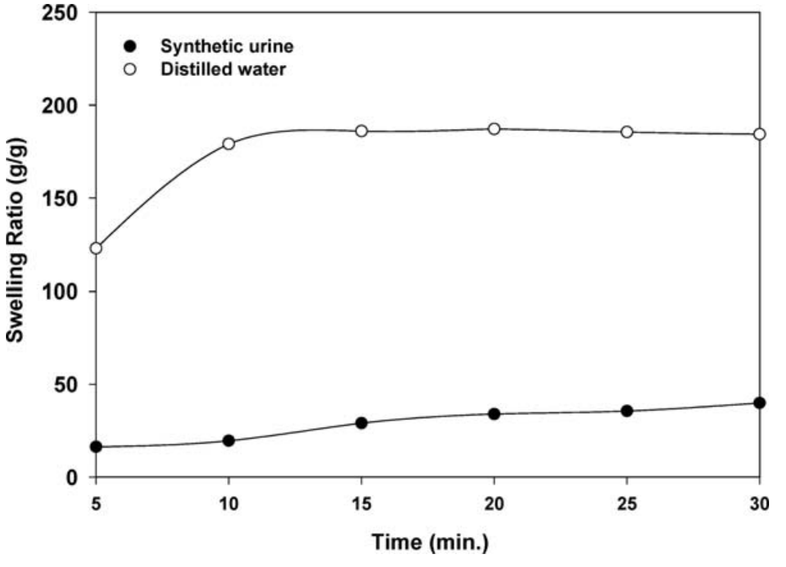

Figure 11. The swelling ratio of CMC-Na/PAAm super-absorbent in synthetic urine and distilled water.

degradation rate was dependant on the crosslinking density and the hydrogel composition. As the PAAm content increases in the copolymer the degradation rate decreases.

The hydrogels are degraded by the microbial action of the different soil flora. Such microorganisms could ingest the carbon molecules of the polymer backbone through enzymatic promoted process giving CO_2 as a final product (25). Thus, it can be concluded that hydrogels formed from CMC-Na and PAAm could belong to the general class of environmentally friendly materials.

Conclusions

Preparation and characterization of crosslinked CMC-Na/PAAm materials were investigated. The gel content and swelling properties of the prepared hydrogel depend on the polymer composition and applied irradiation dose. Using a blowing agent during the radiation crosslinking process enhanced the CMC-Na/PAAm pore structure. The high

Table 1
Biodegradability of the (CMC-Na/PAAm) samples at different compositions for different times

(CMC-Na:PAAm) composition	%Weight loss after burring for different times (days)			
	15	30	45	60
(80/20)	20	39	65	92
(70/30)	15	24	58	85
(50/50)	8	19	43	70

liquid absorbency in such a short time scale for the hydrogel depends on the pore structure and open channels of the prepared hydrogel. The biodegradation of CMC-Na/PAAm hydrogel suggested that such materials may belong to a class of environmentally friendly materials and may be used, practically, as super-absorbent materials in health care products.

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