Hydrogel of Biodegradable Cellulose Derivatives. II. Effect of Some Factors on Radiation-Induced Crosslinking of CMC

RADOSLAW A. WACH,[1] HIROSHI MITOMO,[1] FUMIO YOSHII,[2] TAMIKAZU KUME[2]

[1] Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu, 376-8515, Japan

[2] Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki-machi, Takasaki-shi, Gunma-ken, 370-1292, Japan

ABSTRACT: The effects of high-energy radiation on sodium carboxymethylcellulose (CMC) with a degree of substitution of 2.2 were investigated. Moderate CMC concentrations formed hydrogels by intermolecular crosslinking. Significant influences on the results of irradiation, in addition to the concentration, were the dose and dose rate and the presence of oxygen in the surrounding atmosphere. Up to a 95% gel fraction was obtained from 50 and 60% CMC solutions irradiated by an electron beam. CMC hydrogels swelled by absorbing more than 800 g of water per gram of dry gel at a low applied dose. Swelling tests of CMC hydrogels in salt solutions and in media of various pHs showed that the swelling decreased with the salt concentration and was lower at acidic pH values. Radiation yields of crosslinking and scission were calculated on the basis of gel–sol analysis. Crosslinked CMC, in the form of the hydrogel, was degraded by the action of cellulase enzyme, thereby entering the class of environmentally friendly polymers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3030–3037, 2001

Key words: irradiation; hydrogels; carboxymethylcellulose; crosslinking; biodegradation

INTRODUCTION

Cellulose, as a principal component of plant mass, is the most widely encountered natural polymer. In its structure, the reactivity of the three hydroxyl groups at positions 2, 3, and 6 of the glucosyl unit offers a variety of possibilities for making useful derivatives of this raw material. Among them, cellulose ethers are used extensively. In these derivatives, the hydrogen atoms of the hydroxyl groups of cellulose are partially replaced by alkyl or substituted-alkyl groups. Partial investigations of the radiation chemistry of such compounds have already been completed. Polysaccharides, including cellulose derivatives, generally degrade under ionizing radiation.[1–3] However, some evidence of radiation-initiated crosslinking under special conditions has been reported.[4,5]

At a certain concentration range, water-soluble polymers in solution can be crosslinked by high-energy radiation in the form of hydrogels, which are insoluble in water.[6] They swell significantly, absorbing a huge amount of solvent, but still maintain their initial shape and present some mechanical resistance. With respect to the results of the irradiation of polymers in water solutions, factors such as the polymer concentration in solution, the dose and dose rate, the presence of oxygen, and chemically active additives have an

important impact. Hydrogels formed by irradiation techniques have found applications in many fields, such as biomedical devices.[7–9]

A very desirable class of materials used for common purposes are biodegradable plastics and polymers. Recently, they have attracted the interest of many laboratories. Products made with them should not only fulfil their task excellently but, after use and disposal, should degrade easily in the soil by the action of naturally occurring microorganisms. Biodegradable plastics modified by high-energy radiation are under detailed study.[10] In a previous study, it was found that biodegradable ethers of cellulose, namely, carboxymethylcellulose (CMC), of a high degree of substitution (DS) and at a high concentration can be effectively crosslinked to the form of a hydrogel.[5] In this investigation, the effects of the aging time, concentration, and dose rate on the crosslinking of CMC with a DS of 2.2 (CMC 2.2) in aqueous solutions under ionizing radiation were examined. The radiation yield, swelling behavior, and biodegradability of crosslinked CMC were evaluated.

EXPERIMENTAL

Materials

The sodium CMC 2.2 used in our experiments was a commercial product obtained from Daicel Co., Ltd. (Hyogo-ken, Himeji-shi, Japan). The weight-average molecular weight of CMC was determined by viscosity measurements on the basis of the Mark–Houwink equation (for details, see ref. 11) to be 5.22×10^5 Da. Buffers (pH = 1.68–10.01) used in the swelling experiments were purchased from Kanto Chemical Co., Inc. (Chuo-ku Nihonbashi, Tokyo, Japan). The cellulase enzyme C-0901, from *Penicillium funiculosum*, was obtained from Sigma Chemical Co. (St. Louis, MO). The polymer was used without purification; all other chemicals were analytical-grade.

Sample Preparation and Irradiation

Water was mixed homogeneously with an appropriate amount of polymer with a blending machine. The prepared material was kept for a few days at room temperature to ensure complete dissolution and uniform distribution of polymer chains. Higher concentration solutions were very thick and semisolid gumlike gels. The mixture

was sealed in polyethylene bags or poly(vinylidene chloride) packages for air-free irradiation, after degassing by a vacuum machine. Concentrations are presented as polymer/water (w/w) ratios $\times$ 100%. Solid samples were sealed before irradiation in glass vials after the elimination of air.

Irradiation was carried out with a γ ^{60}Co source at a dose rate of 10 or 1 kGy/h at inert or elevated temperatures. Alternatively, a 2-MeV electron-beam (EB) accelerator was applied with the following irradiation parameters: current = 1 mA, voltage = 1 MeV, and dose per pass = 2.5–10 kGy.

Gel Content, Swelling of Hydrogel, and Yield of Crosslinking and Scission

The gel fraction and swelling of the CMC hydrogel were determined gravimetrically. The gel content in the dried, crosslinked CMC was estimated by the measurement of the insoluble part after immersion in deionized water for 7 days at room temperature. During that time, the soluble part, the sol, was extracted from the gel. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (Gd/Gi) \times 100 \qquad (1)$$

where G_i is the initial weight of dried CMC after irradiation and G_d is the weight of the insoluble part after extraction with water.

The swelling of the crosslinked CMC was estimated according to Japan Industrial Standard K8150. The dried gel was immersed in deionized water or NaCl aqueous solutions of various concentrations of the salt or buffers at different pH values at room temperature. The hydrogel was weighed after the equilibrium of swelling had been reached. With G_s defined as the weight of the hydrogel in the swollen state, swelling was calculated as follows (in grams of absorbed solvent per gram of dried gel):

$$\text{Swelling} = (Gs - Gd)/Gd \qquad (2)$$

Radiation yields of crosslinking and scission were calculated with the Charlesby–Rosiak equation by sol–gel analysis[12] (a specially designed computer program for sol–gel analysis was kindly provided by Dr. J. M. Rosiak of the Institute of Applied Radiation Chemistry, Lodz, Poland).

Biodegradation

Enzymatic degradation was carried out in an acetic acid–NaOH buffer, at pH 5.0, by a cellulase

Table I   Viscosity of CMC Irradiated at a 20 kGy Dose in a Solid State at Various Temperatures Measured After Dilution to 1% Solution at 25°C

Irradiation Conditions	Viscosity (cps)
Room temperature, vacuum	25.7
60°C, vacuum	11.2
100°C, vacuum	5.8

Viscosity of unirradiated 1% solution of CMC = 140 cps. 1 cps = 10^{-3} Pa · s.

enzyme from *P. funiculosum*. About 10 mg of a dried film of the gel, with a thickness about 0.3 mm, was immersed in the enzyme solution (2.5 mL) for a given time. The concentration of the cellulase enzyme in the buffer solution was 0.1 mg mL^{-1}. Tests were performed at the most appropriate temperature for the enzyme activity (37°C) with shaking. After incubation, the samples were washed and kept in an excess of distilled water to wash away degraded polymer and then were dried at 35°C *in vacuo*. The result of enzymatic degradation is expressed as the percentage of weight loss:

$$\text{Weight loss } (\%) = Ge/Gd \times 100\% \qquad (3)$$

where G_e and G_d are the weights of the films after and before enzymatic tests, respectively.

RESULTS AND DISCUSSION

Irradiation of CMC in the Solid State

The results of the interaction of high-energy radiation with polymers depend on many parameters, including the radiation itself, the irradiation conditions, and the nature of the polymer. CMC, possessing in its backbone β-glycosidic linkages, is very susceptible to breakage, resulting in a diminishing molecular weight. The molecular weight of CMC, irradiated in the solid state and in a diluted aqueous solution at room temperature, declines with absorbed energy.[5] The data presented in Table I indicate that the viscosity of solutions and, consequently, the molecular weight of CMC 2.2 irradiated in the solid state at a fixed dose of 20 kGy changed because of the temperature at which the irradiation was conducted. The viscosity dropped radically at the higher temper-

ature of γ processing, even *in vacuo*, when degradation per peroxide was excluded. This is the opposite of the results for the irradiation of poly(ϵ-caprolactone), a synthetic thermoplastic polymer that crosslinks more easily at elevated temperatures, when its chain mobility is enhanced.[13] For CMC, temperature elevation accelerates degradation.

Effect of Aging on the Crosslinking of CMC

For highly viscous solutions or pastelike materials, such as those used in this study, a certain time is necessary to achieve the complete dissolution of a polymer after it is mixed with water. A simple test was done to elucidate an optimal time for irradiation. Samples were γ-irradiated after storage for different times at room temperature. The results are shown in Figure 1. The maximum of the gel part was obtained for samples irradiated 6–10 days after the preparation of the solution. Material irradiated up to 5 days after preparation produced lower gel contents. After the mixing of the components, the material was not homogeneous: it contained regions of low polymer concentration next to parts where the polymer comprised the main part and imbibed water made up only a few percent. The two phases are plainly visible. Thus, the presence of a colloidal material was the prime cause of anomalies in the irradiation results. After several days, the division disappeared, and the mixture became uniform. Then, the irradiation was performed. Long standing times for the solution caused partial degradation of the polymer, consequently lessening the obtained gel fraction. Therefore, all solution sam-
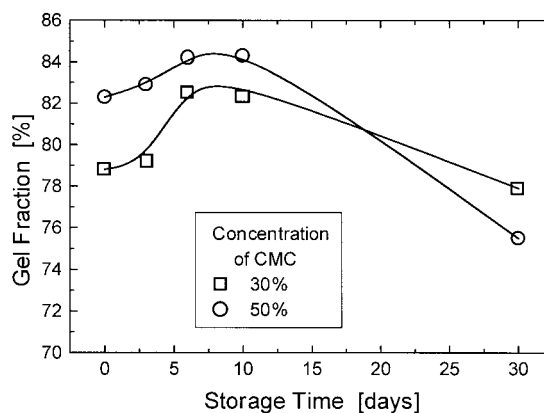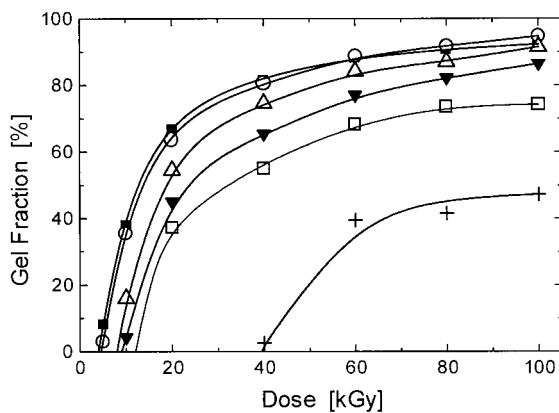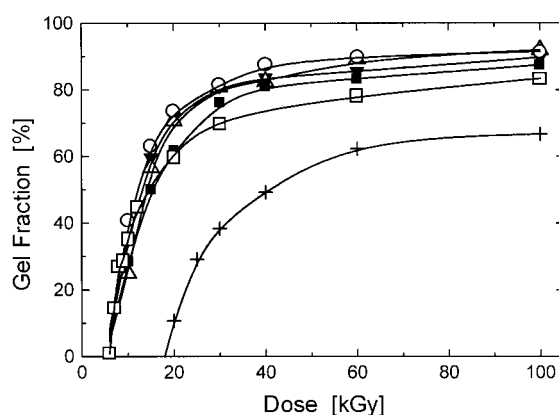

Figure 1   Gel fraction of CMC 2.2 crosslinked by γ rays at a dose of 30 kGy after storage time following solution preparation.

(a)

(b)

Figure 2   Effect of the CMC 2.2 concentration [(■) 60, (○) 50, (△) 40, (▼) 30, (□) 20, and (+) 10%] in an aqueous solution on the gel fraction irradiated by (a) an EB and (b) γ rays in the absence of air.

ples were γ-irradiated or EB-irradiated after 6 days of storage at room temperature.

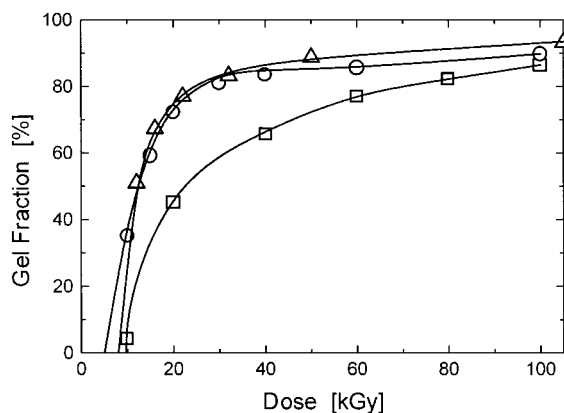## Effect of Concentration on the Crosslinking of CMC

The effect of the CMC concentration in an aqueous solution on the gel fraction is presented in Figure 2 for the polymer treated by an EB and by γ rays in an air-free atmosphere. Plots representing EB-irradiated samples indicate that the gel fraction rises sharply just after exceeding the gelation dose and later levels off. The maximum value of the gel fraction increases with increasing concentration and is highest, about 95%, for polymer concentrations of 50 and 60%. A similar situation is observed for samples irradiated by γ rays, as shown in Figure 2(b). In that case, 50% is

the critical concentration of CMC in an aqueous solution for which the gel fraction reaches the maximum, about 90%. Sixty-percent solutions exhibit a lower gel fraction, 85%, but the distinction in the value of the maximum gel fraction among the investigated concentrations is less for γ-irradiated samples than for EB-irradiated samples. The solutions with concentrations of 20–60% form 80–90% gel by γ treatment, whereas EB-irradiated samples of the same concentration range consist of 75–95% gel. The results are more dependent on the polymer concentration for irradiation with accelerated electrons.

The effect of the dose rate on the gelation behavior of CMC 2.2 in 50 and 30% aqueous solutions is shown in Figure 3(a,b), respectively. Plots representing γ-irradiated samples under an air-free condition at the dose rate 10 kGy/h exhibit
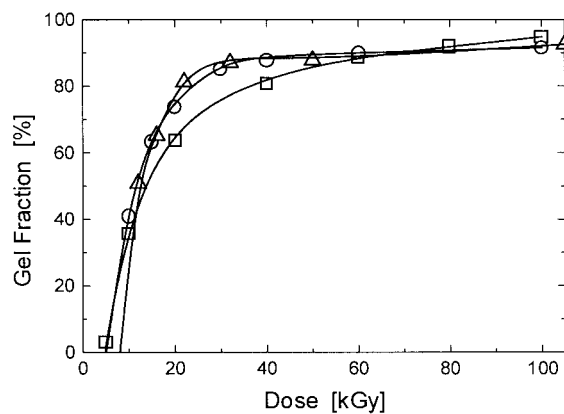
(a)

(b)

Figure 3   Effect of the dose rate on CMC 2.2 crosslinking in (a) 50 and (b) 30% aqueous solutions due to the irradiation dose: (□) EB; (○) γ rays, 10 kGy/h; and (△) γ rays, 1 kGy/h.
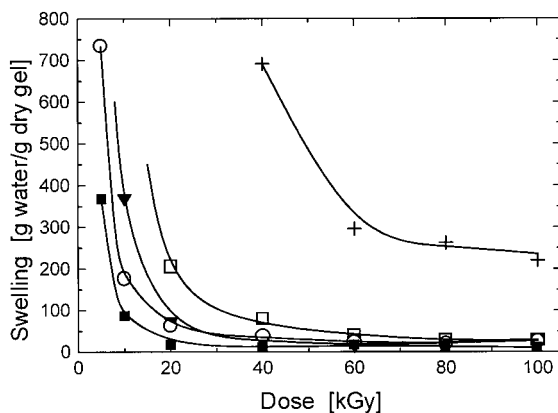
Figure 4 Swelling of the CMC 2.2 hydrogels formed from aqueous solutions by an EB with CMC concentrations of (■) 60, (○) 50, (▼) 30, (□) 20, and (+) 10%.

nearly the same shapes with that irradiated at a dose rate 10 times lower. Gel forms faster at the initial stage of irradiation at a lower dose rate of γ rays. γ irradiation at both dose rates produces the maximum gel fraction, as high as 90%, and it is only slightly dependent on the concentration, whereas EB-processed samples, as stated previously, are more concentration-dependent. From a technological point of view, the irradiation of a 30% aqueous solution of CMC [Fig. 3(b)] by γ rays with a dose rate between 1 and 10 kGy/h is more favorable. To reach about 85% gel, only 40 kGy is required, whereas for EB irradiation, nearly 100 kGy is necessary. Additionally, an EB, even with high energy, has a range of material penetration limited to a few centimeters. It is much less than that for γ radiation. Problems with heat accumulating could also appear. The main advantage of EB treatment in this study is the short processing time and consequent avoidance of degradation through oxides and peroxides, which are present when CMC is processed by γ rays in an air atmosphere. The irradiation of CMC at a high dose by a beam of accelerated electrons with an energy of 1 MeV resulted in a similar gel content for irradiation conducted both *in vacuo* and in air atmosphere.

Swelling of CMC Hydrogel

A comparison of hydrogel swelling, as grams of water absorbed by 1 gram of dried gel, formed from CMC aqueous solutions by EB is shown in Figure 4. All curves present the same tendency. Swelling is highest just after the dose oversteps the gelation point and radically decreases with

increasing absorbed energy at the early stages of gel formation; then, the decreasing becomes slower but is still observable. At the beginning of gelation, the hydrogel is very weak and vulnerable but, because of a relatively low number of intermolecular bonds, is able to expand by absorbing and holding solvent in its voids. With a subsequently increasing dose, the gel content increases, the crosslink density grows, and the hydrogel becomes more tightly packed and firm. Hence, the water sorption ability lessens.

The highest swelling of CMC irradiated at 50% by an EB, 177 was found at a dose of 10 kGy with a reasonable value of the gel fraction, 35%. At an earlier stage of gelation, at a dose of 5 kGy, swelling exceeds 700, but the gel part is only 3.1%. Thus, taking into consideration the mass of the gel fraction that is able to soak up solvent, we find that the amount of water is one-third of that absorbed by 35% gel. This pattern exemplifies that not only is a high value of swelling important but also how much crosslinked material, which only can absorb and keep a solvent, is present. The most advantageous hydrogel, from the point of view of its applications to medical and pharmacological fields, is that combining a high gel fraction, close to 100%, with a crosslinked network strong enough to maintain its shape and significant swelling. Usually, a well crosslinked gel with a stable shape and a high gel fraction does not swell as much as one possessing a lower gel fraction and a weaker structure caused by a limited number of intermolecular bonds. For CMC, the previous assertion is also valid. CMC irradiated at a dose slightly over that causing gelation after swelling is in the form of a slurry without any specific shape. It probably consists of microgels, such as intramolecular crosslinked chains with a limited number of intermolecular bonds. They are unable to permeate through a 200 mesh but can through a 38 mesh.

CMC hydrogel is very sensitive to the presence of even a small amount of salt or a difference in the pH value. This can be explained by the fact that CMC is a polyelectrolyte, so its hydrogel maintains this feature. The equilibrium uptake of a NaCl solution by CMC hydrogel formed from a 50% aqueous solution with an EB at different doses is compared in Figure 5. Samples after irradiation were dried and examined without prior extraction of sol. The degree of swelling decreases continuously with the increasing ionic strength of the solution. For the examined range, 5 mM to 1M NaCl, the total amount of absorbed solvent is 75
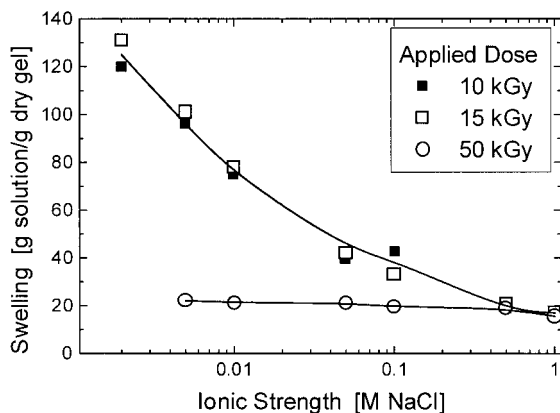
Figure 5 Equilibrium swelling of a CMC hydrogel in NaCl aqueous solutions of various ionic strengths. The gel was prepared from a 50% CMC aqueous solution by an EB at various doses.

and 53%, respectively, of that of deionized water absorption. Swelling in 5 mM and 1M NaCl solutions of CMC samples irradiated at a low dose, 10 kGy, by γ rays at 50% concentration is only 58 and 11%, respectively, of the swelling value in pure water. In accordance with the Donnan equilibrium theory, with rising ionic strength, the distinction in the concentration of mobile ions between the gel and solution is reduced.[14] Therefore, the osmotic swelling pressure of the mobile ions inside the gel decreases, and so the hydrogel collapses.

The influence of solutions of various pHs on CMC gels is depicted in Figure 6 for samples after the extraction of the sol and drying. The equilibrium of swelling of the three hydrogels produced
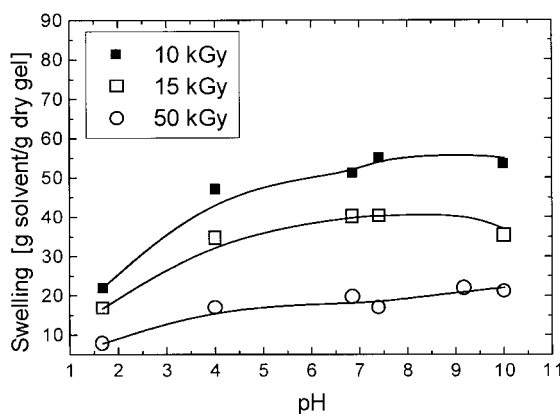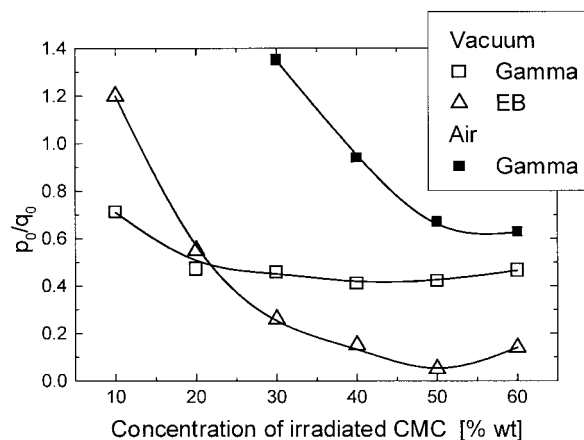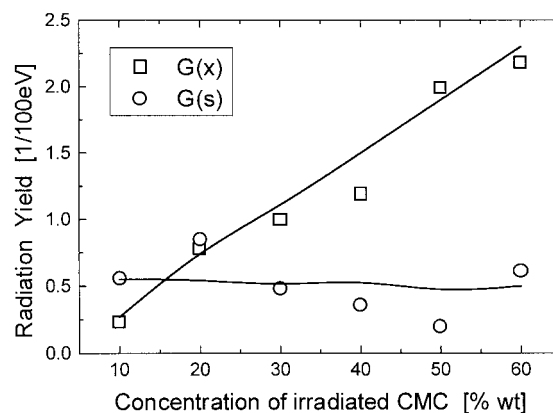

Figure 6 Equilibrium swelling of a CMC hydrogel in aqueous solutions of several pH values. The gel was prepared from a 50% CMC aqueous solution by an EB at various doses.

(a)

(b)

Figure 7 (a) p_0/q_0 ratio of CMC after irradiation and (b) absolute values of crosslinking and degradation yields of CMC irradiated by an EB in an aqueous solution.

by an EB from a 50% aqueous solution of CMC is presented as a function of pH. In general, the material swells in inverse relation to the applied dose: the lower the dose, the higher the swelling. The swelling of hydrogels increases with the pH value; it is lowest in a solution of pH 1.7 and highest in an alkaline medium. The swelling capacity is directly related to both osmotic pressure and electrostatic repulsion according to the level of dissociation. In an acidic medium, no dissociation occurs, molecules are neutralized with sodium or hydrogen atoms attached to oxygen by ionic bonds, and collapsing is observed. With increasing pH, a dissociation of ionic bonds takes place, which is most pronounced in the pH range 2–4: the expansion of the hydrogel is observable. Further neutralization causes only a slight en-

largement of swelling and stabilization at a pH value over 6.5. Then, the electrostatic interaction of ionized carboxyl groups results in uncoiling of the polymer chains, and swelling is the highest. Ionization allows the hydration of charged oxygen atoms, which also provoke solvent absorption by hydrogen bonds and van der Waals interactions. The swelling of hydrogels at pH values near neutral, 6.86 and 7.41, is much less than that in deionized water because buffers used in our experiments were based on acid–base salt solutions and, as we proved before, CMC hydrogels are very sensitive to salts.

Yield of Radiation Processing

An estimation of the radiation yield of crosslinking and scission provides information characterizing the behavior of polymers under the influence of high-energy radiation. In Figure 7(a), data concerning the ratio of degradation to crosslinking density (p_0/q_0) versus the concentration of irradiated CMC are presented. p_0/q_0 is the parameter that allows the determination of the final results of irradiation and is equal to half of the scission yield/crosslinking yield ratio [$0.5 \times G(s)/G(x)$]. If p_0/q_0 is lower, crosslinking occurs more efficiently. It decreases with concentration for CMC irradiated by γ rays in air because the scission yield decreases, leading to the highest gel fraction at polymer concentrations of 50 and 60%. For irradiation in an oxygen-free atmosphere, p_0/q_0 is much less and remains at the same level, 0.41–0.47, except for the lowest concentration, 10%, for which both radiation yields are small and the maximum gel fraction is lower [cf. Fig. 2(b)]. This is due to the fact that primary radicals from water radiolysis are more prone to recombine with themselves before they come across rare polymer chains.

The number of radicals created in the system at the same time is much higher for an EB than for γ irradiation. Under these conditions of EB irradiation, the concentration of radicals differs by about 500 times with respect to γ rays at a dose rate of 10 kGy/h. Crosslinking reactions prevail over degradation, more so for irradiation at a high dose rate, resulting in an enhancement of the maximum value of the gel fraction, especially for increasing concentrations. This becomes evident through a comparison of p_0/q_0 ratios. For concentrations 30% and greater, the density of degradation to crosslinking is significantly lower for samples irradiated by an EB than by γ rays. It is most pronounced for 50% CMC solutions when the yield of scission is only 10% of the yield of crosslinking. In this situation, gel formation is the most effective. The absolute values of the yields of crosslinking and scission for an example of CMC solutions treated by an EB are presented in Figure 7(b). The yield of scission, $G(s)$, remains at the same level. However, the yield of crosslinking grows progressively throughout all examined concentrations. This is the reason for increasing the maximum of the gel fraction for the most concentrated solutions, as can be seen in Figure 2(a).

Enzymatic Degradation of CMC Hydrogel

Plastic materials commonly used in everyday life have become recently very troublesome to the environment. To solve this problem, researches are paying special attention to novel biodegradable polymers. Polymers that can be converted to carbon dioxide, water, and energy are called environmentally friendly. Degradable commercial polymeric materials are limited to aliphatic polyesters, polyethers, and some polysaccharides, among which cellulose derivatives are widely used. Glycosidic linkages bonding polysaccharide rings are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Degradation is a desirable feature of hydrogels used in medicine as controlled drug delivery systems, in agriculture as superabsorbers, and elsewhere. Most hydrogels with a high water-absorption capacity prepared from synthetic polymers are difficult to decompose naturally. Therefore, cellulose ethers such as CMC are especially suitable for those purposes.

Tests carried out by the cellulase enzyme C-0901 from *P. funiculosum* in an acetic acid–NaOH buffer (pH 5.0) prove the high degradability of CMC. The results are presented in Figure 8 for hydrogels prepared with different doses of γ rays, 50 and 30%, with CMC aqueous solutions. A blank test in the buffer solution without the enzyme diminished the mass of CMC material no more than 5%. If we take into consideration the applied dose, the tendency to decompose for the two investigated concentrations of CMC is identical. A hydrogel of a lower crosslinking density degrades faster than that crosslinked more tightly by higher energy because the number of intermolecular bonds is far greater in the latter. Samples formed from 50 and 30% solutions by 15 kGy degrade completely after 95 and 72 h, respec-
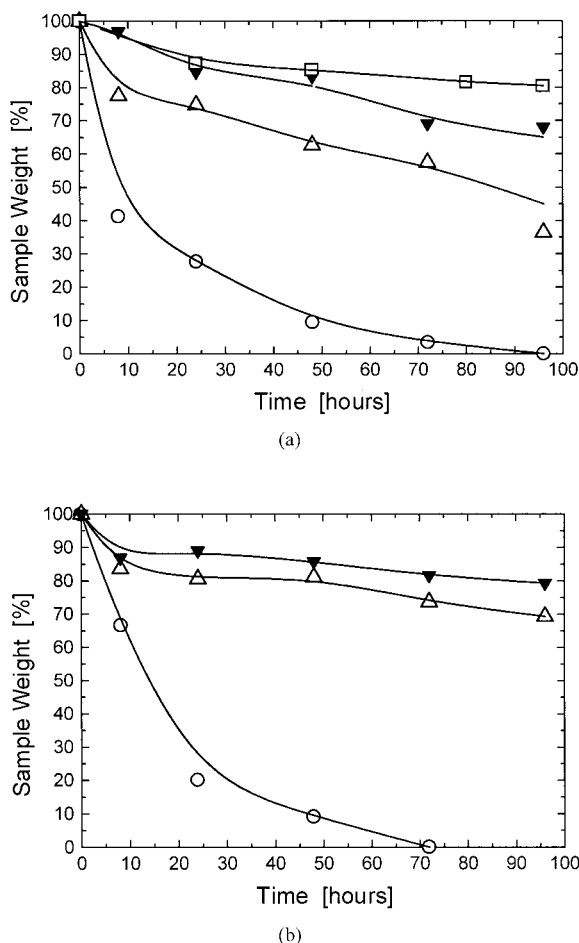
(a)

(b)

Figure 8 Biodegradation of crosslinked CMC by the cellulase enzyme C-0901 from *P. funiculosum* in an acetic acid–NaOH buffer (pH 5.0). Hydrogels were prepared from (a) 50 and (b) 30% CMC aqueous solutions at different doses of γ irradiation: ($\bigcirc$) 15, ($\triangle$) 40, ($\blacktriangledown$) 60, and ($\square$) 100 kGy. The degradation of hydrogels did not exceed 5% for tests without the enzyme.

tively. Those formed by 10 kGy disappear before 8 h of incubation and possess a relatively high gel fraction, 41 and 35% gel for 50 and 30% CMC, respectively. Gels irradiated at a dose of 40 kGy and above the degrees of degradation do not exceed 50% after 96 h of incubation.

On the basis of these results, we can state that CMC hydrogel is highly degradable. The material, characterized by its strong swelling ability when irradiated at lower doses, which are very desirable from the point of view of further applications, degrade by enzymatic action, the fastest kind of disintegration.

CONCLUSION

Hydrogels of CMC 2.2 were prepared by the radiation initiation of γ rays and an EB. The influence of the dose rate, the irradiation atmosphere, and other factors was investigated. Moderately and highly concentrated solutions irradiated by an EB and γ rays, without access to air, formed gel fractions up to 90–95% and were characterized by a low degree of scission throughout all reactions initiated by the ionizing radiation. The ratio of the yields of scission and crosslinking was lowest for highly concentrated solutions irradiated by an EB, and the gelation process was most effective. The presence of air during irradiation increased the yield of scission and, consequently, diminished the maximum gel fraction. Swelling of the obtained hydrogels varied because of the initial concentration of the solution and the applied dose. Gels just above the gelation point possessed the highest sorption capacity. Swelling decreased in salt solutions and in an acidic medium. Enzymatic tests proved that CMC hydrogels characterized by high swelling are biodegradable and, therefore, are not harmful to the environment.

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