Transactions of the Materials Research Society of Japan 32[3] 713-716 (2007)

Preparation and Properties of CMC Gel

Machiko Takigami, Haruyo Amada, Naotsugu Nagasawa*, Toshiaki Yagi*, Takamitsu Kasahara**, Shoji Takigami** and Masao Tamada*
Gunma Industry Support Organization, c/o Environmental Polymer Group, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292
Fax: 81-27-346-9694, e-mail: takigami.machiko@jaea.go.jp
* Environmental Polymer Group, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292
Fax: 81-27-346-9694, e-mail: nagasawa.naotsugu@jaea.go.jp
** Center for Material Research by Instrumental Analysis, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515
Fax:81-277-30-1141, email:takigami@chem-bio.gunma-u.ac.jp

Abstract
Novel elastic gel was obtained by immersing paste of sodium carboxymethylcellulose (CMC) in acid solution. The paste was prepared by mixing CMC and water at the concentration of 20%. Water absorption and mechanical strength of the resultant gel were evaluated after removing uncrosslinked CMC and acid. Combination of radiation crosslinking and the immersion in acid resulted precise molding and dimension stability of the gel. Maximum mechanical strength of the gel at 50% compression increased with acid concentration for the unirradiated and the irradiated samples at 5-20kGy. The gel prepared by irradiation at 5-10kGy and the immersion did not cause rupture after 50% compression and was more than 100 times stronger than the radiation-crosslinked gel. The reason of the mechanical strength was attributed to crosslinks formed by the acid treatment. The crosslinks by the irradiation had been referred to chemical bonds, whereas, those by acids were caused by hydrogen bonds, which was elucidated by FT-IR, ICP and TG-DTA measurements. Sodium in the carboxymethyl groups is replaced by hydrogen in the acid solution. The hydrogen bonds induced the decrease of CMC solubility in water and formed the elastic gel.
Key words: Carboxymethylcellulose, Radiation, Crosslinking, Acid, Mechanical properties

1. INTRODUCTION

Carboxymethylcellulose (CMC) is a water-soluble polymer having various application fields such as civil engineering, oil drilling, fish feed, food additives, pharmaceuticals, cosmetics, and textile printing. The usage can be extended by crosslinking CMC molecules by chemicals or by ionizing radiation to highly concentrated aqueous solutions[1-5]. As crosslinking agents are toxic in general, the method is not favored to prepare gel. In radiation-induced gels, a high degree of water absorption can be achieved, and not only crosslinking but also degradation of CMC molecules takes place simultaneously. Too high water absorbency at low doses and too high crosslink density at high doses cause poor mechanical properties of the hydrogel. The gel is fragile and brittle. As the result, the use of the radiation-induced hydrogel was limited to the fields that required very high water absorbency.

We have found that the CMC forms gel when mixed with acid, replacing sodium in CMC with hydrogen to form hydrogen bonds[6]. The resultant gel showed elasticity and higher mechanical properties. However, molding of the samples was not easy because of the too quick reaction. Use of acid solution with high concentration caused hardening of the samples in short time. The application of the method might contribute to improve the strength of radiation induced CMC hydrogel and easier molding of the gel.

2. EXPERIMENTAL

2.1 Materials

Carboxymethylcellulose (CMC) 1380 (sodium salt, DS=1.36, Daicel Chemical Industries, Ltd., Japan) was used all through the experiment. The chemicals used were reagent grade and used as received.

2.2 Gelation of CMC

CMC was mixed with pure water using a hybrid defoaming mixer (AR-250, Thinky Cooperation, Japan). The concentration of CMC was 20%. The mixed material, paste, was pressed to form plate with the thickness of 10mm. The CMC plate was sealed into a plastic bag and irradiated with Co-60 γ-rays at a dose rate of 10kGy/h at room temperature. After irradiation, the plate was molded into discs with a diameter of 15 mm. After weighing the discs, they were immersed in acid aqueous solutions with the concentrations of 0.1-1M at room temperature. After some time, the discs were picked up from the acid solution and the discs were immersed in purified water to remove acid and soluble CMC, uncrosslinked CMC. The water was exchanged repeatedly until the conductivity of the water becomes nearly equal to that of pure water. The discs after removing acid and uncrosslinked CMC were dried. The gel fraction and the amount of water absorbed by the gel were defined as follows:

$$\text{Gel fraction (\%)} = 100 \times Wg / Wi$$

where Wi and Wg are the weights of initial dry CMC and insoluble part after extraction with water, respectively.

$$\text{Water absorbed by gel} = (Ws\text{-}Wg) / Wg$$

where Ws is the weight of swollen hydrogel.

2.3 Mechanical properties of gel

Mechanical properties of the gels after immersion in water were measured using a Compact Table-Top Universal Tester (EZ-Test, Shimadzu Co.). Maximum stresses at 50% compression were measured for the gels.

2.4 Sodium content in gel

The amount of sodium contained in gel was evaluated with an inductivity coupled plasma atomic emission spectrometry (ICP, Optima 4300DV, Perkin Elmer) after degrading the gel with 69% ultra pure nitric acid.

2.5 FT-IR

FT-IR spectra of the gels were measured by Magna 560 + ContinuμMII (Nicolet, Thermo Fisher Scientific K.K.).

2.6 TG-DTA

TG-DTA measurements were carried out for the samples using EXSTAR6000 Series TG/DTA6200 (Seiko Instruments Inc.) from 30 to 400℃。

3. RESULTS AND DISCUSSIONS

3.1 Gel fraction

All CMC dissolved in water without irradiation and immersion in acid. CMC pastes became insoluble in water after irradiation and/or immersion in acid. The gel fractions when immersed in hydrochloric acid for 4 days followed by removal of acid and uncrosslinked CMC are shown in Fig. 1. Gel fractions increased remarkably with acid concentration for the unirradiated and irradiated samples at 5kGy, however, no significant increase in gel fractions was observed for irradiated samples at higher doses. In irradiated samples, degradation of CMC occurs with crosslinking reaction and low molar mass fractions easily dissolve in water, so that the gel fraction does not increase with dose. According to our former research[6], gelation of CMC occurred when CMC was mixed with acid. Sodium existing as a counter ion of carboxymethyl ion was replaced with hydrogen. In this experiment,

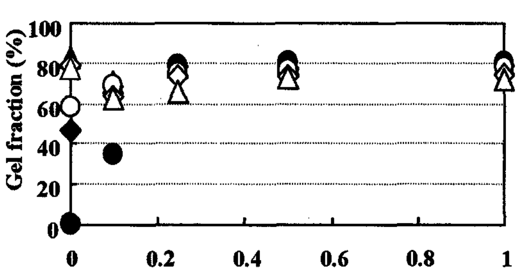

Fig. 1 Gel fraction of irradiated CMC followed by immersion in HCl for 4 days. ●: 0kGy, ◆: 5kGy, ▲: 10kGy, ○: 20kGy, ◇: 30kGy, △: 50kGy.

gelation of CMC by acid takes place by diffusion of acid into the CMC paste. The diffusion of acid and dissolution of uncrosslinked CMC proceed simultaneously, replacing sodium to hydrogen. As the results, solubility of CMC decreases, CMC molecules aggregate, and hydrogen bonds are formed between molecules.

Gel fractions of the samples immersed in 0.5M hydrochloric acid did not change after longer immersion time as shown in Fig. 2. It infers the diffusion of acid is achieved in 1 day.

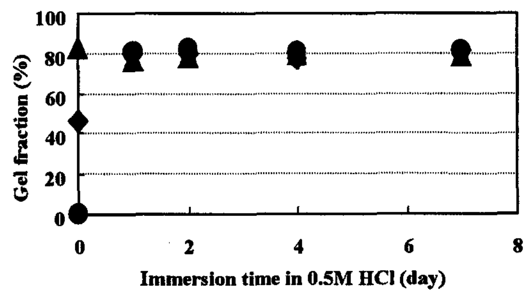

Fig. 2. Gel fraction of irradiated CMC followed by immersion in 0.5M HCl. ●: 0kGy, ◆: 5kGy, ▲: 10kGy.

However, gelation is not too quick by immersing the samples in acid solutions compared to the mixing CMC with acid.

3.2 Water absorption by gel

Water absorption by gel after immersion in water is shown in Fig. 3. Water absorbed by gel decreases with increase of acid concentration both for the unirradiated and the irradiated samples. It implies that crosslinks are formed by immersing the sample in acid, in the same way with our former results[6]; hydrogen bonds are formed by mixing CMC with acid solution. The amount of 0.1 M hydrochloric acid used for the experiment is enough to convert almost all sodium in carboxyl groups to hydrogen.

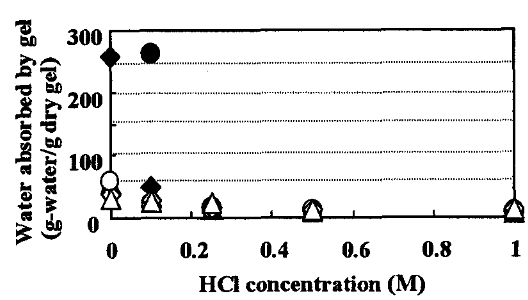

Fig. 3. Water absorption by irradiated CMC gel followed by immersion in HCl for 4 days. ●: 0kGy, ◆: 5kGy, ▲: 10kGy, ○: 20kGy, ◇: 30kGy, △: 50kGy.

As shown in Fig. 4, water absorption decreases gradually with immersion time in acid indicating that the hydrogen bonds are formed gradually. However, the relation between the conversion of sodium to hydrogen and the formation of hydrogen bonds is not clear yet.

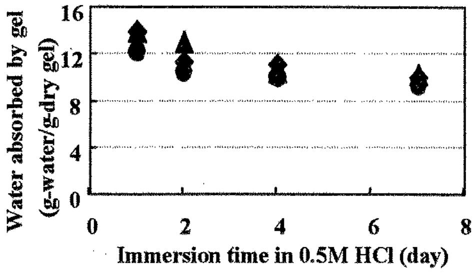

Fig. 4. Water absorption by radiation induced CMC gel followed by immersion in 0.5M HCl. ●: 0kGy, ◆: 5kGy, ▲: 10kGy.

3.3 Mechanical properties of gel

There were not significant differences in the maximum stresses at 50% compression among the radiation induced hydrogels. They were very fragile and brittle. As radiation-induced hydrogels absorb much amount of water, the swelling pressure caused by the immersion of gel into water expands the gels and makes the gels brittle.

The effect of acid concentration on the maximum stress at 50% compression is shown in Fig. 5 for the samples after removing uncrosslinked CMC and acid. The strengths increased with acid concentrations for unirradiated and irradiated samples at 5-30kGy. In 50kGy irradiated samples followed by immersion in 1M hydrochloric acid, the strength of the gel decreased compared to that immersed in 0.5M hydrochloric acid however, some of the samples irradiated at lower doses and immersed in acid did not rupture and kept the shape as shown in Fig. 6. The strength was more than 100 times of that of the radiation-induced hydrogel. Thus, the gel, which can keep 10 times water of the gel weight and is not fragile and not brittle, was obtained by combining the irradiation and the acid immersion methods. Unirradiated and irradiated samples at low doses were stronger than samples irradiated at higher doses. Irradiated samples at 5-10kGy were stronger than unirradiated samples in all acid concentrations examined.

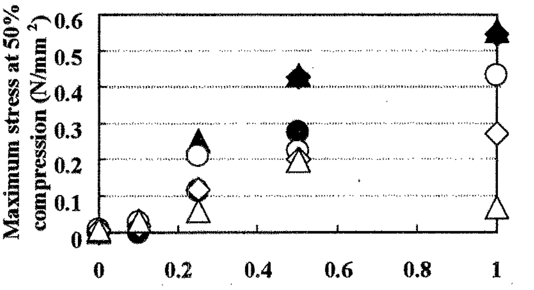

Fig. 5. Maximum stress of gel at 50% compression after immersion in HCl flowed by immersion in water. ●: 0kGy, ◆: 5kGy, ▲: 10kGy, ○: 20kGy,◇: 30kGy, △: 50kGy.

With the increase of doses, the number of crosslinks increases resulting stiff gels at low doses and brittle gels at high doses. Moderate amount of crosslinks is effective to improve the mechanical strength of the gel, however, too many number of crosslinks decreases the mechanical strength. The samples irradiated at 5-10 kGy showed dimensional stability after immersion in hydrochloric acid. In the unirradiated samples, expansion of the gel was observed, whereas the irradiated samples kept the shape after immersion in acid. Most of the samples after removing uncrosslinked CMC and acid ruptured by the 50% compression,

3.4 Sodium contents in gel

Sodium contents in the gels unirradiated and irradiated at 5 and 10kGy followed by immersion in hydrochloric acid were in the range of 0 to 11.6% as shown in Table 1. As the CMC without irradiation and immersion in acid dose not make gel, the sodium content of the CMC is shown for CMC which was dialyzed against deionized water and freeze-dried. Without immersion in acid, sodium content did not change as shown for the irradiated gel at 10 kGy. The result infers that sodium contained in CMC is not replaced only by immersing the sample in water. Acid is necessary to replace sodium with hydrogen.

Assuming that carboxymethyl groups are distributed uniformly in CMC and all the groups are in the form of

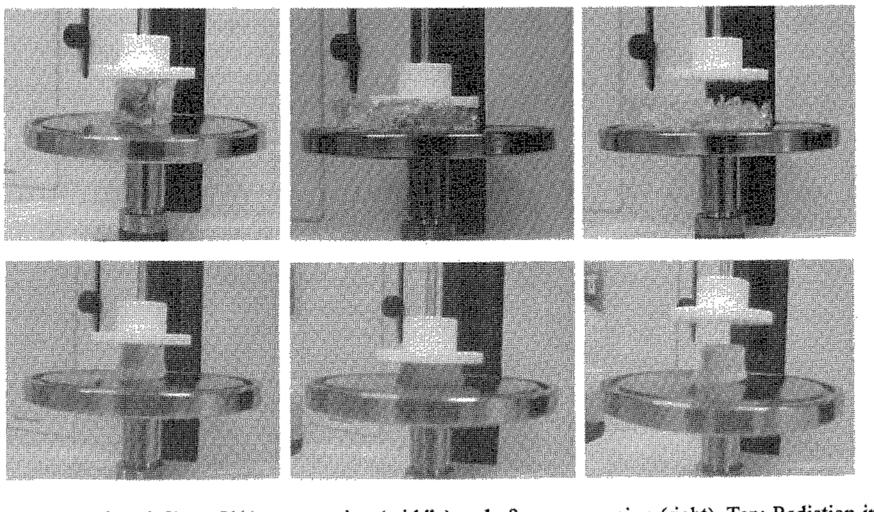

Fig. 6 Gels before compression (left), at 50% compression (middle) and after compression (right). Top: Radiation-induced hydrogel, Bottom : Hydrogel prepared by combination of radiation and acid treatment.

sodium salt in the initial CMC, we can calculate the sodium content in the initial CMC to be 11.6%. The 0.5% sodium content in the gel corresponds to 96% substitution of sodium to hydrogen. Therefore, almost all carboxymethyl groups in the gel become free acid form after immersion in hydrochloric acid for 4 days. The result that the sodium content in the irradiated CMC at 5kGy followed by immersion in 0.5M hydrochloric acid for 1 day was 0.1% infers the quick replacement of sodium to hydrogen in carboxymethyl groups.

Table I Sodium contents in gels after immersion in HCl for 4 days.

HCl concentration (M)	Sodium content (%) Unirradiated	Irradiated 5kGy	Irradiated 10kGy
0	11.0		11.6
0.1	0.5	0.4	0.3
0.25	0.3	0.2	0.2
0.5	0.1	0.1	0.1
1.0	0.1	0.1	0

The amount of water absorbed by the gel decreased with the decrease of sodium content in gel as shown in Fig. 7. Drastic decrease in water absorption was observed in sodium content between 0.4 and 0.5%. The replacement of sodium with hydrogen causes the decrease of solubility in water, however, it does not directly correspond to hydrogen bonding formation as mentioned above. Replacement occurs first and then hydrogen bonds are formed.

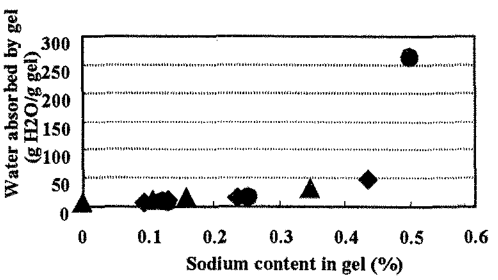

Fig. 7. Relation between sodium content in gel and water absorbed by gel. ●: 0kGy, ◆: 5kGy, ▲: 10kGy.

Substitution of sodium to hydrogen in the gel was proved by FT-IR spectra of samples immersed in hydrochloric acid. Immersion of the sample in the acid made decrease of the absorption attributable to sodium carboxylate around 1600 cm^{-1}. Instead, the absorption by acid form around 1730 cm^{-1} increased as shown in Fig. 8. The spectra are for the irradiated samples at 10 kGy, however, similar results were obtained for unirradiated samples.

3.5 TG-DTA

As shown in Fig. 9, the DTA measurements showed the slight shift of the peak to lower temperature by irradiation. The peak temperatures of the decomposition were lower by 4 and 7℃ in the sample irradiated at 10 and 50kGy than that of the initial CMC, respectively. Broadening and shift of the peak to the higher temperature due to decomposition were observed for

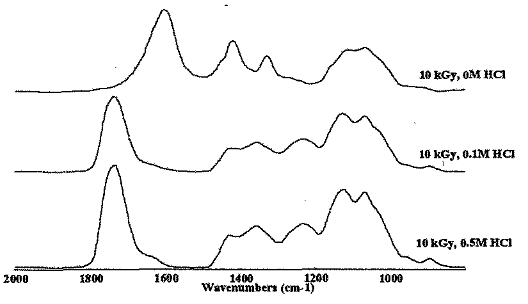

Fig. 8 FT-IR spectra of irradiated samples at 10 kGy followed by immersion in HCl.

10kGy irradiated samples followed by immersion in acid. Almost the same behavior was observed for the unirradiated samples. However, crosslinks induced by radiation did not cause broadening of the peak and shift of the peak to higher temperature. The results indicate that CMC molecules are more restricted in movement after the immersion in acid. Hydrogen bonds formed by the acid immersion caused the restriction. In radiation-induced hydrogel, covalent bonds is formed, however, no broadening and no shift of the peak to higher temperature did occur. The different effects are not elucidated yet.

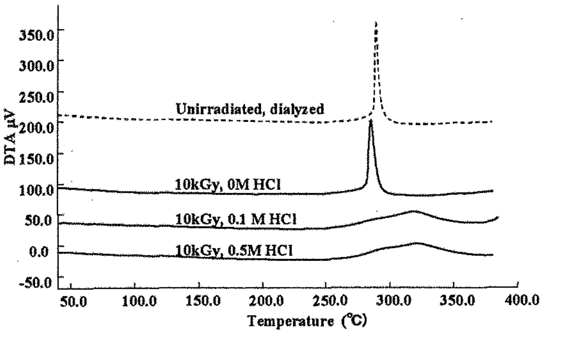

Fig. 9 DTA of unirradiated and irradiated samples at 10kGy followed by immersion in acid.

Acknowledgement

The authors are grateful for the sponsorship of Japan Science and Technology Agency to achieve Gunma Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence.

References

【1】 B. Fei, R.W. Wach, H. Mitomo, F. Yoshii and T. Kume, *J. Appl. Polym. Sci.*, **78**, 278-283(2000).

【2】 R.A. Wach, H. Mitomo, F. Yoshii, and T. Kume, *J. Appl. Polym. Sci.*, **81**, 3030-3037(2001).

【3】. R.A. Wach, H. Mitomo, N. Nagasawa and F. Yoshii, *Rad. Phys. Chem.*, **68**, 771-779(2003).

【4】 P. Liu, M. Zhai, J. Li, J. Peng, and J. Wu, *Rad. Phys. Chem.*,**63**, 525-528(2002).

【5】 K. Hara, M. Iida, K. Yano, and T. Nishida, *Colloids Surf., B*, **38**, 227-230(2004).

【6】 M. Takigami, H. Amada, N. Nagasawa, T. Yagi and M. Tamada, Fiber Preprints, Japan, Vol. 61, No. 3, p.158 (Autumn Meeting, 2006), The Society of Fiber Science and Technology, Japan.

(Received January 20, 2007;Accepted May 10, 2007)