EFFECT OF TEMPERATURE ON THE RADIATION CROSSLINKING OF CARBOXYMETHYLCELLULOSE

PART 1. EFFECT OF ELEVATED TEMPERATURE ON THE RADIATION CROSSLINKING OF CARBOXYMETHYLCELLULOSE

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1. INTRODUCTION

Carboxymethylcellulose (CMC) is the most popular cellulose ether. It is an anionic linear polymer in which original H atoms of cellulose hydroxyl groups are replaced by carboxymethyl substituent – CH_2COO^- [1, 2]. Some attempts for chemical crosslinking of CMC in order to get hydrogel were conducted with divinylsulphone as a crosslinking agent [3, 4]. However, CMC can not be used as itself because a poor efficiency of crosslinking has been achieved. Pure CMC hydrogel without admixture of other polymer and without addition of low molecular weight contaminant can be produced using γ-rays [5, 6]. Hydrogels prepared by radiation technique are not only crosslinked but also sterilized [7]. Hydrogel of CMC can absorb and hold amount of solvent in its network structure and in the point of view of environment, it still retains good property of cellulose to be biodegradable [8].

The results of the interaction of high energy radiation with polymers depend on many parameters including radiation itself, irradiation conditions, and the nature of polymer. Only one study of the effect of temperature during irradiation on the crosslinking of CMC was found in the literature [9]. In this research, the effect of temperature on the radiation crosslinking of CMC samples was investigated, in part 1, we study about the effect of elevated temperature during the time of irradiation on the gel fraction and swelling ratio of CMC.

2. MATERIALS AND METHODS

2.1. Materials

CMC – Na is provided by Daicel Chemical Industry, Ltd. Its degree of substitution is 1.36. The viscosity and molecular weight of CMC are 1820 m.Pa.s and 1.11×10^6, respectively.

2.2. Gamma irradiation and preparation of CMC-Na hydrogel

Deionized water was mixed with an appropriate amount of CMC-Na powder by using a blending machine. The mixture of various concentrations from 5% to 70% were kept for 1 day. 1.5g of the mixture was sealed in the PE bag after degassing by a vacuum machine.

2.3. Heating during irradiation

The PE bags containing degassed mixture were put in screw capped test tubes containing water, then they were irradiated by γ - rays at the doses of 5, 10, 15, 20, 25, 30 and 50 kGy, (dose rate: 10 kGy . h^{-1}), at 25°C, 50°C and 70°C.

Gel fraction and swelling ratio of irradiated CMC samples were determined by a conventional gravimetric procedure. In brief, a preweighed piece of irradiated sample was immersed into a distilled water bath for 48 h at room temperature, filtered with stainless steel net of 100 mesh to get the insoluble part. Then CMC hydrogel was dried at 50°C until constant weight.

The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (Gd / Gi) \cdot 100$$

where Gi is the initial weight of dried sample and Gd is the weight of dried gel. The swelling ratio was calculated according to the following equation:

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

where Gs is the weight of the gel in swollen state. For each experiment with different temperature, dose and dose rate were measured by using alanine dose meter

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of CMC on the crosslinking

Aqueous solution of CMC with the concentration from 5% to 70% (w/w) were irradiated to produce crosslinks. The crosslinking process of CMC in aqueous solution initiated by γ –rays is presented in figure 1. Gel fraction of CMC at the concentration region from 10% to 50% increased with absorbed dose, steeply at the beginning of gelation and later levels off. Maximum gel fraction was achieved at 30% about 90% at the dose of 30 kGy. The results also show that, CMC at concentration of 5% and 70% degraded by radiation. It may be: Chains of CMC at concentration of 5% are separated by water and placed at a distance from each other, that prevents intermolecular reactions to occur. Then the yield of the crosslinking is trivial and the leading radiation -induced reaction is scission of main chain. For CMC at concentration of 70%, it was observed that water is not homogeneously dispersed into CMC. It is important for crosslinking that the polymer is homogeneously dissolved in water. For CMC at concentration of 50%, it was not degraded by radiation, but it was observed that water it seemed not to be homogeneously dispersed into CMC.

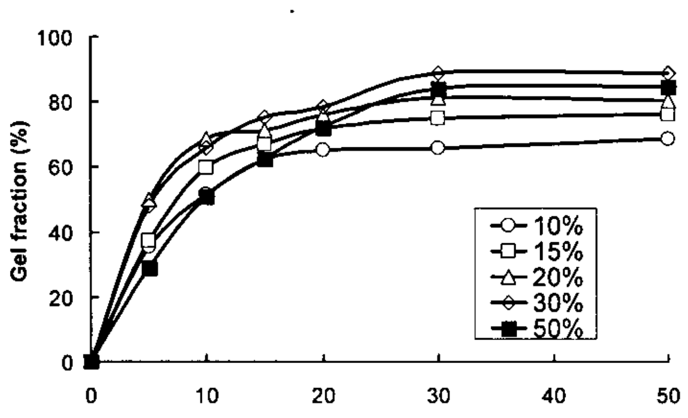

Figure 1. Effect of concentration of CMC on the crosslinking

(CMC samples irradiated at 25°C)

3.2. Effect of concentration of CMC on the swelling ratio

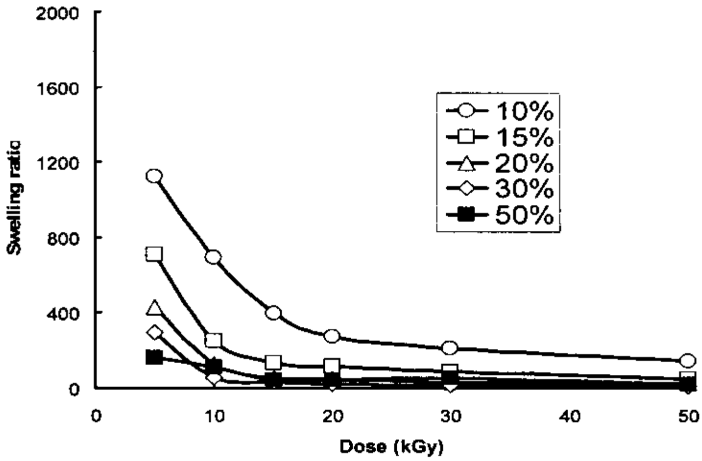

Figure 2. Effect of concentration of CMC on the swelling ratio

The basic feature of hydrogel is its ability to absorb and hold significant amount of solvent in its network structure. Swelling is usually express as grams of water absorbed by 1 gram of dried gel. Figure 2 shows the effect of concentration on the swelling ratio of CMC. All curves present the same tendency. Swelling is the highest just after the dose oversteps the gelation point and radically decreases with increasing of absorbed dose at the early stage of gel formation. Swelling ratio decreases with the increasing of concentration of CMC in solution.

3.3. Gel fraction and swelling ratio of CMC irradiated at 50°C

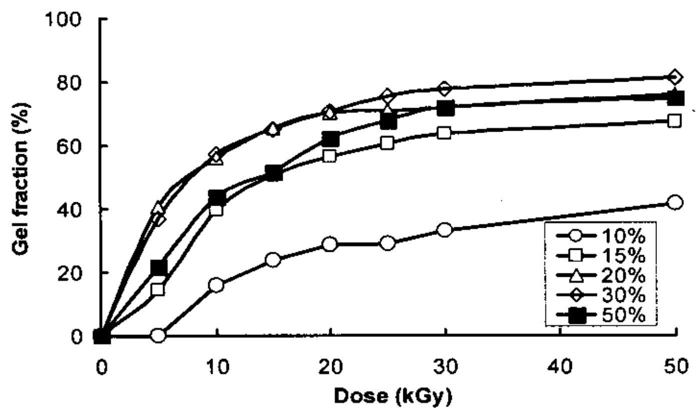

Figure 3. Effect of heating at 50°C on the crosslinking of CMC

The results in figure 3 shows that all curves presented for gel fraction had the same tendency - gel fraction increased with the increasing of doses. Heating at 50°C during irradiation reduced gel fraction but increased swelling ratio as compared to 25°C irradiation, about 1.5 to 3 times higher (Fig. 4). CMC in aqueous solution of 30% formed maximum gel fraction about 80% at the dose of 50 kGy. Irradiated at 50°C, 5%, 70% aqueous solutions of CMC degraded by radiation, and 10% aqueous solution of CMC also degraded at the dose of 5 kGy.

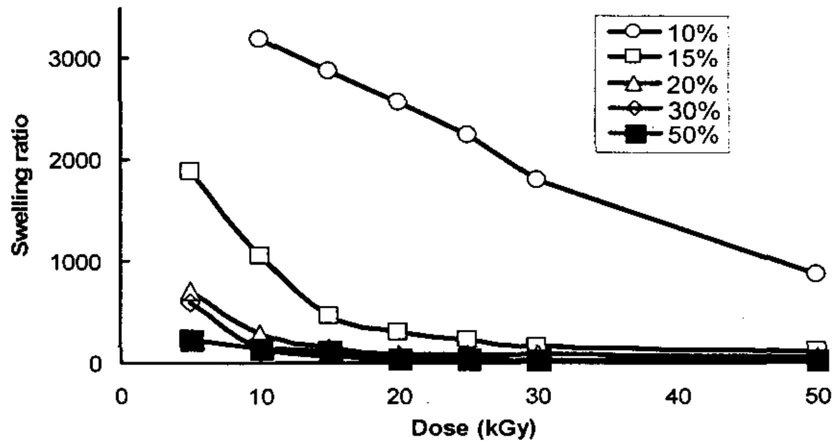

Figure 4. Effect of heating at 50°C on the swelling ratio of CMC

3.4. Gel fraction and swelling ratio of CMC irradiated at 70°C

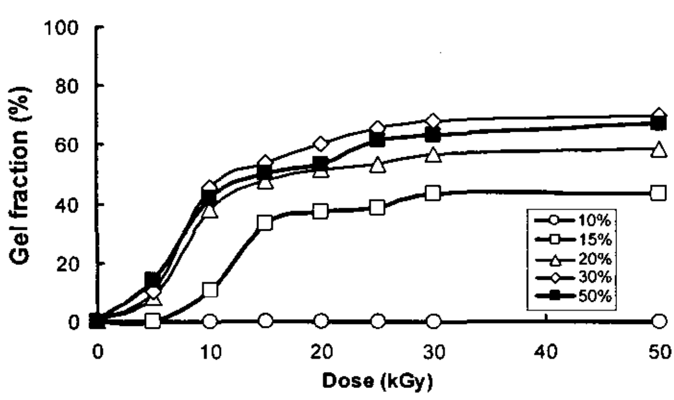

Figure 5. Effect of heating at 70°C on the crosslinking of CMC

Samples of CMC were put at 70°C during irradiation. The results are presented in Fig. 5. CMC in aqueous solutions of 5%, 10%, 70% degraded by radiation. 15% aqueous solution of CMC also degraded at 5 kGy. The gel fractions of CMC irradiated at 70°C were about 10 to 45% lower compared to that obtained from the samples irradiated at 25°C, but swelling ratio was higher comparing to that obtained from samples processed at 50°C and 25°C. It is about 3 to 12 times as much comparing to that obtained at the same dose at 25°C (figure 5). It may be because of low probability of intermolecular recombination of macroradicals. At elevated temperature the life time of macroradicals, radicals may be shorter than that of macroradicals and radicals at room temperature [9].

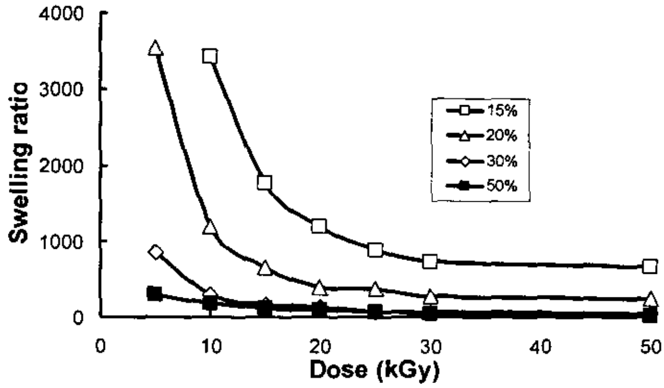

Figure 6. Effect of heating at 70°C on the swelling ratio of CMC

4. CONCLUSIONS

From the above results, some conclusions can be withdrawn as follows:

- CMC in 5%, 70% solutions degraded by radiation at 25°C, 50°C and 70°C.

- CMC in 10% solution also degraded by radiation at 70°C.

- At the temperature region from 25°C to 70°C, from the dose 5 kGy to 50 kGy, the higher temperature the samples were irradiated at, the lower gel fraction was obtained and the lowest gel fraction was obtained from the sample irradiated at 70°C.

- At the temperature region from 25°C to 70°C, from the dose 5 kGy to 50 kGy, the higher temperature the samples were irradiated at, the higher swelling ratio was achieved. The highest swelling ratio gel fraction was achieved from the sample irradiated at the temperature of 70°C.

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ABSTRACT

Gel fraction and swelling ratio of aqueous solution of carboxymethylcellulose (CMC) with the DS of 1.36 irradiated at various concentrations from 5% to 70% at temperature of 25°C, 50°C and 70°C were determined. 5% and 70% aqueous solutions of CMC degraded by radiation at 25°C, 50°C and 70°C. Gel fraction of CMC at the concentration region from 10 to 30% increased with the increasing of concentration and with absorbed dose. 50% aqueous solution of CMC formed low gel fraction compared to 30% aqueous solution of CMC at the dose of 30 kGy. At the temperature region from 25°C to 70°C, the highest gel fraction was achieved from the sample irradiated at the temperature of 25°C, but the highest swelling ratio was obtained from the sample irradiated at the temperature of 70°C.

TÓM TẮT

ẢNH HƯỞNG CỦA NHIỆT ĐỘ LÊN KHẢ NĂNG KHÂU MẠCH CỦA CARBOXYMETHYLCELLULOSE (CMC) BẰNG BỨC XẠ

PHẦN 1. ẢNH HƯỞNG CỦA SỰ TĂNG NHIỆT ĐỘ LÊN KHả NĂNG KHÂU MẠCH BẰNG BỨC XẠ CỦA CMC

Độ khâu mạch và độ trương của Carboxymethylcellulose (CMC) dưới ảnh hưởng của bức xạ γ và sự thay đổi nhiệt độ trong thời gian chiếu xạ đã được nghiên cứu. CMC ở nồng độ 5% và 70% bị cắt mạch ở nhiệt độ 25°C, 50°C và 70°C. CMC ở nồng độ 10% bị cắt mạch khi chiếu xạ ở nhiệt độ 70°C. Độ khâu mạch của CMC gia tăng với liều chiếu xạ và đạt tối đa tại liều 30kGy. Ở dải nồng độ từ 10 đến 30%, độ khâu mạch của CMC tăng theo nồng độ của CMC và đạt tối ưu ở 30%. Trong dải nhiệt độ từ 25°C tới 70°C, ở cùng 1 liều chiếu, nhiệt độ càng tăng, độ khâu mạch càng giảm ngược lại độ trương càng tăng.

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